# THE STUDY OF SURFACE PHYSICO-CHEMICAL PROPERTIES OF ALCOHOL-WATER MIXTURES USING REVERSE-FLOW GAS CHROMATOGRAPHY

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**FACULTY OF SCIENCE**
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**KUALA LUMPUR**

**2015**

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DISSERTATION
SUBMITTED IN
FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

2015

# UNIVERSITI MALAYA

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Registration/Matric No: SGR120052

Name of Degree: MASTER OF SCIENCE

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

THE STUDY OF SURFACE PHYSICO-CHEMICAL PROPERTIES OF ALCOHOL-WATER MIXTURES USING REVERSE-FLOW GAS CHROMATOGRAPHY

Field of Study: PHYSICAL/ENVIRONMENTAL SCIENCE

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# ABSTRACT

Spillage of volatile chemicals such as organic solvents into aquatic environment via various industrial activities has been a growing major worldwide concern. These volatile chemicals may spread into the atmosphere via evaporation and diffusion. Evaporation is a process where a substance in liquid phase is converted into the vapor phase. Reversed–flow gas chromatography (RF-GC) technique which is one of the perturbation gas chromatography techniques was used to determine the rate coefficient for evaporation and diffusion coefficients ($D$) of selected alcohols. The main objectives of this study are to determine the effect of water on the evaporation of alcohols from water-alcohol mixture, to study the influence of temperature, concentration of alcohol and carbon number on the evaporation of alcohols from water-alcohol mixture, and to study the effect of surfactant concentration and the types of surfactant (nonionic, cationic and anionic surfactant) on the evaporation of selected alcohols.

With the presence of water, the $K_G$ values of methanol and ethanol were largely reduced and it was due to the formation of hydrogen bond between water and alcohol molecules. As most of the evaporation process, the rate of evaporation of selected alcohols from alcohol-water mixtures was also found to increase with temperature. In addition, ethanol and 1-propanol were found to be more volatile than methanol and 1-butanol for the pure alcohol liquid and even with the presence of 5% water. With the presence of 10% water, 1-propanol showed the highest $K_G$ as compared to methanol, ethanol and 1-butanol.

The $K_G$ values pure methanol and ethanol were largely reduced by the addition of Triton X-100 which is a nonionic surfactant. This result was due to the formation of insoluble surfactant layer that covered the surface of the alcohols and reduced the rate of

alcohols evaporation. The effect of nonionic surfactant, anionic surfactant and cationic surfactant on the evaporation of methanol from 24% methanol in water were evaluated using Triton X-100, SDS and CTAB, respectively. The result showed that Triton X-100 and CTAB can be used to reduce the methanol evaporation. However, the addition of SDS into the 24% methanol in water was found to enhance the methanol evaporation from the methanol-water mixture.

In conclusion, RF-GC can be a good method and instrumentation for the measurement of the rate of evaporation for alcohols. RF-GC is unique because of its simplicity in the measurement of $K_G$ since the time taken to acquire the data is less than 3 hours. Furthermore, this method enables the measurement of $K_G$ and $D$ for the volatile liquids simultaneously. In addition, this study also showed that nonionic and cationic surfactant can be a good candidate to reduce the evaporation of hazardous methanol from methanolic wastes.

# ABSTRAK

Kesedaran yang tinggi terhadap pencemaran bahan kimia mudah meruap seperti bahan-bahan pelarut organik ke dalam persekitaran akuatik melalui pelbagai aktiviti industri telah meningkat di seluruh dunia. Bahan-bahan kimia mudah meruap ini boleh tersebar ke atmosfera melalui penyejatan dan penyerapan. Proses penyejatan ialah proses di mana bahan yang pada asalanya berada dalam keadaan cecair berubah menjadi wap. Teknik kromatografi aliran berbalik (TK-AB) yang mengaplikasikan teknik kromatografi gas aliran terganggu digunakan bagi menetu ukur kadar penyejatan ($K_G$) dan menganggarkan pekali resapan ($D$) bagi alkohol terpilih. Objektif utama untuk kajian ini adalah untuk menentukan kesan air terhadap penyejatan alkohol daripada campuran air-alkohol, mengkaji kesan suhu, kepekatan alcohol dan bilangan karbon alkohol terhadap penyejatan alkohol daripada campuran air-alkohol, dan mengkaji kesan kepekatan surfaktan dan jenis surfaktan (bukan ionic, kationik dan anionic) terhadap penyejatan bagi alkohol yang terpilih.

Nilai $K_G$ bagi methanol dan ethanol adalah sangat berkurangan dengan kehadiran air disebabkan pembentukan ikatan hidrogen di antara molekul air dan molekul alkohol. Pekali kadar penyejatan bagi alkohol yang terpilih didapati meningkat dengan peningkatan suhu seiring dengan kebanyakan proses penyejatan. Tambahan pula, ethanol dan 1-propanol didapati lebih cepat meruap berbanding dengan metanol dan 1-butanol dalam keadaan cecair tulen dan pada kehadiran 5% air. 1-propanol menunjukkan nilai $K_G$ tertinggi jikan dibandingkan dengan metanol, etanol dan 1-butanol dengan kehadiran 10% air.

Nilai $K_G$ untuk metanol dan etanol tulen telah dapat dikurangkan dengan nilai yang besar dengan kehadiran Triton X-100 yang merupakan surfaktan bukan ionik. Keputusan ini adalah disebabkan pembentukan lapisan surfaktan yang tidak larut yang

menutup permukaan alkohol dan mengurangkan penyejatan alkohol. Kesan surfaktan bukan ionik, anionik dan kationik terhadap penyejatan metanol daripada larutan 24% metanol telah dinilai masing-masing menggunakan Triton X-100, SDS dan CTAB. Hasil kajian menunjukkan Triton X-100 dan CTAB boleh digunakan untuk mengekan penyejatan metanol. Walau bagaimanapun, penambahan SDS ke dalam larutan 24% methanol didapati telah menyebabkan peningkatan penyejatan metanol daripada campuran metanol-air.

Kesimpulannya, TK-AB adalah suatu kaedah dan peralatan yang berguna bagi mengukur kadar pekali penyejatan bagi alkohol. TK-AB adalah unik disebabkan ianya mudah untuk mengukur nilai $K_G$ disebabkan masa yang diperlukan bagi memperolehi data adalah kurang daripada 3 jam. Selain itu, kaedah ini juga membolehkan nilai $K_G$ dan $D$ bagi cecair mudah meruap dapat ditentukan dalam masa yang sama. Tambahan pula, kajian ini juga menunjukan bahawa surfaktan bukan ionik dan kationik merupakan surfaktan yang sesuai bagi mengurangkan kesan penyejatan yang merbahaya alkohol daripada sisa-sisa metanol.

# ACKNOWLEDGEMENTS

This dissertation was carried out at the D306, Centralized Equipment Laboratory, Chemistry Department, Faculty of Science, Universiti Malaya, at first, under the supervision and guidance of Associate Professor Dr. Rashid Atta Khan, towards whom I express my deepest gratitude for the knowledge and the help that he offered me throughout the stages of my master studies.

I also thank Dr. Tay Kheng Soo for his help in many-sided minor issues concerning the writing of this dissertation, as well as Prof Dr. Sharifuddin Md. Zain for his participation in my advisory committee.

I am grateful to Institute for Postgraduate Studies (IPS), Universiti Malaya for granting me Skim Biasiswazah for master studies. The work was also supported by a Postgraduate Research Grant (PPP) No. PG067-2013A from Institute of Research Management and Monitoring (IPPP), Universiti Malaya. The author wants to dedicate his appreciation to the staff from the Library, University of Malaya for helping to provide some of the articles.

I pay my thanks to Mr. Khalisanni Khalid (Pakar Umum at Malaysian Agricultural Research and Development Institute (MARDI) cum Bright Sparks Scholarship holder for doctoral studies) for his kindness in learning some concepts of Reversed-Flow Gas Chromatography (RF-GC) and motivating me to publish my articles in Impact Factor (IF) journals.

I am thankful to Professor Dr. Sharifuddin Md. Zain, Mr. Ir. Moovarasen from Fisher Scientific Malaysia and Mr. Khalisani Khalid as well as financial support from Dr. Tay Kheng Soo for their help in re-constructing Reversed-Flow Gas Chromatography.

*Dedicated to my dearest mother for her blessings,*
*sisters, friends and*
*Associate Professor Dr. Rashid Atta Khan (UM: 2006-2012)*
*Thank you Allah and Peace be upon you, Muhammad(P.B.U.H.)*

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| | |
|---|---|
| $a_L$ | Cross sectional area in liquid column |
| atm | Atmosphere |
| $c(l', t_0)$ | Concentration of analyte gas at $x = l'$ and time $t_0$ |
| $c_0$ | Equilibrium solute concentration in the liquid phase |
| $c_1, c_2, c_3$ | Concentration of solute at the detector, when double reversal of carrier gas is made (as shown in general sampling Equation (2.2) |
| cf. | compare/see/refer to |
| $c_z$ | Concentration of a solute vapor in the diffusion column |
| $^{O}C$ | Degree Celcius |
| $CH_3OH$ | Methanol |
| $C_2H_5OH$ | Ethanol |
| cm | Centimeter |
| $Co_3O_4^-$ | cobalt oxide ion |
| $D$ | Mutual diffusion coefficient of two gases |
| $D_{AB}$ | Binary diffusion coefficient of the solute-solvent pair |
| $\delta(x-l')$ | Dirac delta function |
| $\frac{\partial c}{\partial z}$ | Concentration gradient |
| e.g. | for example |
| EPA | Environment Pollution Agency |
| et. al., | and friends |
| exp | exponential function |
| FSG | Fuller-Schettlar-Giddings |
| g/mol | gram per mol |

| | |
|---|---|
| GC | Gas Chromatography |
| $\Delta H$ | Change in enthalpy of adsorption |
| $\Delta S$ | Change in entropy of adsorption |
| $\Delta E$ | Differential in molar internal energy of the gas and liquid |
| $h$ | Height of a sample peak measured from the ending baseline |
| $h_\infty$ | Infinity peak height defined by Equation (3.3) |
| i.d. | internal diameter |
| $J$ | The number of moles passing through a unit area in unit time |
| K | Kelvin |
| $K_{\mathrm{G}}$ | Rate of coefficient for evaporation of liquid |
| $l', l$ | Lengths of two sections of sampling column |
| $L$ | Length of diffusion column |
| $m$ | Response factor of the detector, FID |
| mN/m | mili Newton/meter |
| M | Molar |
| M | Molecular weight |
| MeOH | Methanol |
| ml | Millimeter |
| mmHg | millimeter mercury |
| N | Avogadro's number |
| $n_{\mathrm{v}}, n_{\mathrm{l}}$ | Number of molecules per milliliter in the vapor and the liquid |
| -OH | Hydroxyl |
| p | Total pressure |
| ρ | Density |
| $P\Delta V$ | Work done by vapor in expanding to a volume $\Delta V$ |
| $\Delta P$ | Change in pressure |

| | |
|---|---|
| $\frac{r_L}{r_G}$ | Ratio of the liquid phase resistance to gas phase |
| $R$ | Gas constant |
| RF-GC | Reversed-Flow Gas Chromatography |
| $r_L, r_G$ | Ratio of the liquid phase resistance to gas phase |
| $\boldsymbol{\Gamma}$ | Surface concentration |
| S | Cross sectional area of the column |
| SDS | sodium dodecyl sulfate |
| $t$ | Time variable |
| $t'$ | Time interval of backward flow of carrier gas |
| $t_M$ | Hold-up time, or dead time |
| $t_R$ | Retention time defined by $\mathrm{t_R} = \frac{1}{\mathrm{v}}\,(1+\mathrm{k}) = \mathrm{t_M}(1+\mathrm{k})$ |
| $t_0$ | Time measured from the beginning to the last backward reversal of gas flow |
| $T$ | Time defined by $\tau = \mathrm{t} - \mathrm{t_R}$ |
| $T$ | Temperature |
| TK-AB | Teknik gas Kromatografi Aliran Berbalik |
| $\bar{U}$ | Average solvent (carrier gas) velocity |
| v | Linear velocity of carrier gas in the interparticle space of the column |
| V | Volume of carrier gas passed through the column |
| $\dot{\mathrm{V}}$ | Volume flow-rate of carrier gas |
| $V_L$ | Volume of the liquid |
| $\boldsymbol{\gamma}$ | obstructive factor |
| $\boldsymbol{\sigma}$ | Collision diameter |
| $\boldsymbol{\sigma}_t$ | Standard deviation in time units |

| | |
|---|---|
| $\Omega_{12}$ | Collision integral depending on the temperature and the interaction energy of colliding molecules |

# CHAPTER 1

# INTRODUCTION

## 1.1 Pollution and Evaporation

Pollution is not a new phenomenon of the twentieth first century. It has been recorded continuously. The magnitude of the pollution has increased and been recognized more widely, and simultaneously with the industrialization and the growth of urban populations. Evaporation plays a major role in ecological fate when volatile pollutants are introduced into aquatic environments by accidental spills, industrial effluents, or directly into the air from the sources such as bioreactors, cooling towers of nuclear plants and etc. (Gavril et al., 2006). More than 99.9% of dry atmosphere air consists of nitrogen, oxygen, and argon with only about 0.1 % remaining for carbon dioxide, krypton, neon, helium, and xenon. Also, trace gases (such as $CH_4$) are also present in atmosphere. Atmospheric air may contain 0.1 to 5% water by volume (States and Gardner, 2000). All other compounds (solid, liquid, or gaseous substances that change the natural atmospheric composition) that enter the air from different sources are classified as pollutants (Berezkin and Drugov, 1991). The recent reported industrial accident of methanol spillage makes the study of the impact of the alcohol on environment significance to be addressed (Mohammad et al., 2013). Evaporation emerges as important process that taking part on the air-water interphase and thus, encourages us to contribute on this particular field by acquiring data that can benefit the environmental researcher in future. This study focused on the determination of rate coefficients and diffusion coefficients of liquids such as alcohol. These parameters provide important information on the transfer of pollutants from the air to water or vice versa.

Short chain alcohol for example, methanol and ethanol can be used as the transportation fuel (Bechtold et al., 2007), which are considered as sustainable fuel resources (Granda et al., 2007) as compared to the fossil fuels. The alcohol based fuel will become a compromising fuel for transportation in future since there is highly research in converting biomass into useful alcohols (Dutta et al., 2012; Tan and Dutta, 2013). The demand of ethanol especially in United States has increased dramatically in the last ten years because of the demand for ethanol-blend fuels. In order to fulfill the increasing demands for ethanol, 204 bio refineries in 29 states in United States are able to produce 13 billion gallons in 2010 (Dinneen, 2011). 75% of U.S. gasoline was blended with 10% ethanol and 90% gasoline (E10) (SEIG, 2011). Thus, the study of the physical and chemical properties of the short chain alcohols needs to be carried out in order to understand their impact to the environment.

24 % methanolic waste by weight is considered as dangerous to the human health by U.S. Environment Protection Agency, USEPA (USEPA, 1994; MI, 2014). The wastes are usually discarded to the water environment and can cause the direct or indirect effect to the human's health. Most literatures discussed on the effect of the alcohols related to the use of alcoholic beverages.

The information given is largely focused on long term exposure by ingestion (Eckardt et al., 1998; Giovannucci et al., 1993; Husain et al., 2001; Nogueira et al., 2014; Pohorecky, 1991; Singletary and Gapstur, 2001).The exposure of the short chain alcohol on human health can be divided into two, i.e. short term (acute) and long term (chronic) effects (Bechtold et al., 2007). Short term (acute) effect can cause headache, nausea, vomiting, drowsiness, fatigue and coma. Ethanol can cause irritation to eyes and the respiratory system at concentration 5 000 – 10 000 ppm. On the other hand, the long term effect will cause the progressive liver dysfunction and cirrhosis with the chronic ingestion of 2 g/kg/day. The ability of low molecular weight to be the alcohol-blend fuels may

encourage the liquid to be transferred around the world using the land and water transportations. Most of the denatured ethanol is largely transported from production factory by rails and thus, making the ethanol as number one hazardous material transported by rails (Rudolph, 2009). Highly production and transportation of ethanol in U.S. since 2000 have caused 26 significant fires, 5 train derailments, and 3 ethanol tanks fires (Rudner, 2009). Besides that, the recent industrial spillage accident of methanol occurred in Malaysia involving the explosion of one PETRONAS ship (Mohammad et al., 2013).

The understandings of the properties of low molecular alcohol (e.g. methanol) can quickly guide actions to be taken by the respective authorities, such as applying a suitable surfactant to curb the methanol from being evaporated into the air – this effort will help prevent the people nearby from inhaling the hazardous vapors such as methanol from the environment (Mohammad et al., 2013).

## 1.2 Evaporation and Diffusion coefficient

### 1.2.1 Evaporation

Evaporation which occurs only on the surface of liquid is a type of vaporization process. The liquid surface is a dynamic system where the liquid molecules tend to resist any modification on the surface by establishing the attractive interaction between them. The attractive forces between the liquid molecules at the surface are illustrated in the Figure 1.1.

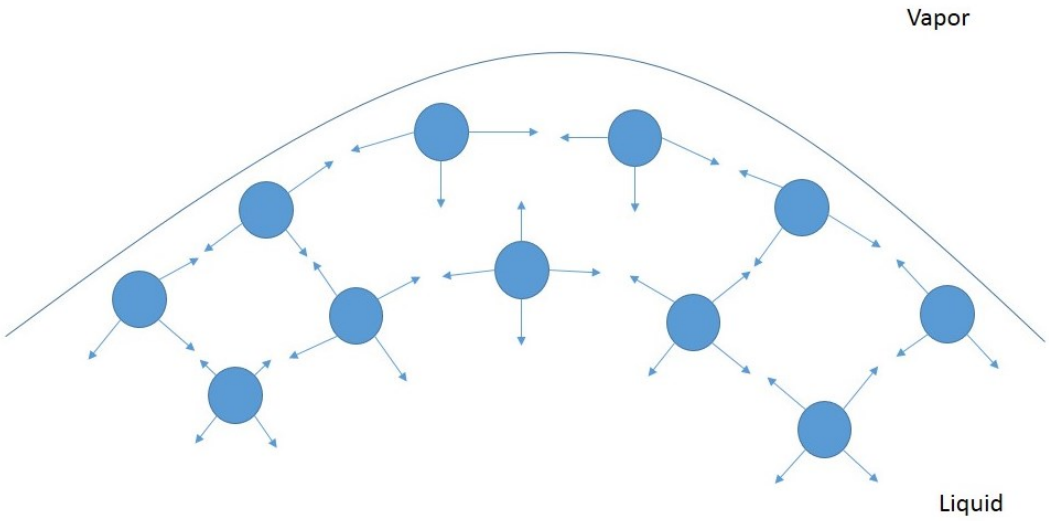



**Figure 1.1:** Attractive forces (represented by arrows) between alcohol's molecules (show as spheres) at the surfaces and in the interface of a liquid (Davies and Rideal, 1961).

Evaporation is also a type of phase transition or phase change. It is a process where molecules in a liquid phase become gas (for example, water vapor). In order for the evaporation to occur, the molecules at the liquid's surface must overcome the strong attraction forces between molecules. Thus, the molecules require kinetic energy which with a function of temperature to overcome the potential energy of attraction from neighbouring molecules. If the process occurs at the constant volume, the molecules will obey the following equation 1.1(Rastogi and Misra, 1978):

$$\frac{n_v}{n_l} = e^{\frac{\Delta E}{RT}}$$

(1.1)

where, $n_v$ is the number of molecules per milliliter in the vapour, $n_l$ is the number of molecules per milliliter in the liquid, $\Delta E$ is the difference in molar internal energy of the gas and liquid, $R$ is the gas constant, and $T$ is the absolute temperature. Equation 1.1 illustrated the ratio between the numbers of molecules in the vapour phase to the number of molecules in liquid phase. The most important criteria for the evaporation to occur is the rate at which heat is supplied to the liquid must be high enough to provide the latent heat of vaporization. The molecules need to acquire enough kinetic energy in order to overcome the attraction forces from the other molecules, so that they will evaporate from the liquid's surface. Since the kinetic energy of a molecule is proportional to the temperature, the evaporation process proceeds more quickly at higher temperatures. As the molecules possess enough kinetic energy to counter the attraction forces between the molecules on the surface of the liquid, the molecules will escape from the neighboring molecules that have a lower average kinetic energy, and consequently, the temperature of the liquid's surface will decrease. Therefore, the average kinetic energy of the remaining molecules are decreased. Thus, heat must be transferred from the bulk liquid to the liquid's surface in order to equilibrate the temperature within the liquid. The process will proceed until the whole liquid achieved a new thermal equilibrium.

The measurement of rate for evaporation of this work was done at constant pressure, specifically atmospheric pressure (101325 Pa). This approaches will be differed from what has been deduced before in which the evaporation process are assumed to occur at the constant volume (Brennan et al., 1974; Peiss, 1989). Thus, equation that relates the energy to evaporate one mole of liquid with the internal energy of the system is required for calculating the evaporation rate of the liquid under study at a constant

pressure. This relationship is given by the first law of thermodynamic (Rastogi and Misra, 1978):

$$\Delta H = \Delta E + P\Delta V \tag{1.1}$$

where, $\Delta H$ is the molar heat of vaporization, $\Delta U$ is the difference in molar internal energy of the gas and liquid and $P\Delta V$ is the work done by vapor at constant atmospheric pressure which resulting volume expansion ($\Delta V = \Delta V_{gas} + \Delta V_{liquid}$). Substitution of $P\Delta V$ with $RT$ into Equation 1.2 yielded Equation 1.3. The latent heat of vaporization ($\Delta H$) can be calculated by assuming the gas is obeyed the ideal gas law and the molar volume of the liquids is negligible by comparing to that vapour (Rastogi and Misra, 1978).

$$\Delta H = \Delta E - RT \tag{1.2}$$

$\Delta H$ is a function of temperature that can be measured by calorimeter at the normal boiling point, $\Delta E$ is the difference in molar internal energy of the gas and liquid, $R$ is the gas constant and $T$ is the absolute temperature.The evaporation process can be observed by the gradual disappearance of a liquid from a container. This can be measured when the liquid level in a container declines over time. Besides that, the evaporation process becomes significantly higher with high air flow rates between the gaseous and liquid phase or on liquid's surface with high vapor pressure. The movement of air just above the liquid surface will be swept along the vapor that is newly evaporated and thus providing revenue for other liquid molecules on the surface to escape. Generally, three elements that will influence the evaporation process are heat, air/surroundings humidity and air movement. The other factors that can influence the evaporation process are described as follow:

- **Concentration of the evaporating substances in the air above the liquid's surface** - When the air above the liquid is saturated with evaporating substances, then the liquid molecules at the surface will evaporate more slowly.
- **Concentration of other substances in the air** - When the air is already saturated with other substances, the air will have a lower capacity to access the molecule on the surface to evaporate.
- **Concentration of other substances in the liquid (impurities)** - When the liquid contains other substances (e.g. impurities), it will influence the attraction force between the molecules. The perturbation of the orientation of the molecules will influence the average kinetic energy that required for the molecules at the surface to evaporate.
- **Inter-molecular forces (attraction forces and repulsion forces between molecules)** - The stronger attraction forces over repulsion forces between the molecules at the surface will cause the molecules to stay in the liquid state. Therefore, higher heat energy is needed for the molecules to escape from the surface.
- **Pressure** - Pressure exerts on the liquid's surface will hinder the molecules on the surface to escape from the bulk liquid phase. The evaporation process proceeds faster at the surface with lower pressure.
- **Surface area** (Gavril et al., 2006) - A liquid with a larger exposed surface area will evaporate faster than the smaller one. A larger exposed surface area will increase the population of the molecules at surface and hence, increases the probability of the molecules to escape from bulk liquid phase.
- **Density** - Mathematically, density is defined as mass divided by volume:

$$\rho = m/V \tag{1.3}$$

where, $\rho$ is the density, $m$ is the mass and $V$ is the volume. Higher density suggests the mass of a liquid increases faster than its volume. The mass of a liquid plays a vital role in

determination of evaporation rate. Previous researcher such as Heen (1913) has found that the quantity of liquid evaporated was proportional to the product of the vapor pressure and molecular weight. The relationships between the evaporation rates and molecular weight of evaporating liquid are established by Hofmann (1932) according to the following equation 1.5:

$$\text{Evaporation rate} = \text{Vapour pressure} \times \text{molecular weight} / 11 \tag{1.4}$$

Since one mole of a pure substances (in this case liquid) has mass that equal to its molecular weight in grams, thus, there is a direct relationships between the molecular weight of a liquid and mass of a substance. A substance is denser because the inter-molecular bonds in the liquid bulk are particularly strong. It will hold the molecules together more closely and the evaporation rate becomes lesser since more energy is required to break the bond between the molecules. Furthermore, there is a relatively few molecules in the liquid possess enough kinetic energy at a given temperature in order to escape from the surface. On the other hand, if a substance is denser because the molecular weight is greater, the average molecule's velocity which depends on its kinetic energy (KE) is lower. Kinetic energy of a molecule in a substance can be described as the following relationship:

$$\text{Kinetic Energy, KE} = 1/2mv^2 \tag{1.5}$$

In average, the kinetic energy for all molecules in a substance is about the same. Thus, relatively few molecules with heavy molecular weight, populated on the surface, can possess enough velocity (which converted from average kinetic energy) to completely escaped from the surface of the liquid. In conclusion, the higher the liquid's density, the slower the liquid molecules on the liquid's surface evaporates.

• **Monolayer thickness or the effect of monomolecular films at liquid gas interphase** - Previous researchers have found a related monomolecular film which is believed to be markedly reduced the rate of evaporation of water (Jarvin et al., 1962; Langmuir and Langmuir, 1927; Rideal, 1925). The adsorption of the monomolecular film at the air-water interface is possible since the monomolecular film features the properties such as low permeability in water, closely packed orientation at the interface and having a high intermolecular cohesion. For example, liquid paraffin is considered as the most effective monolayer to retard the evaporation of water (Jarvin et al., 1962). The liquid paraffin features a high degree of adlineation between the adjacent, saturated aliphatic chains which enhances the retardation effect. Besides that, the monomolecular film also plays a vital role in determining the temperature at the water surface. The rate of evaporation of water is measured on the rate of the heat loss from the water surface to the atmosphere. The greater the rate of evaporation of water, the greater the transfer rate of heat from water surface to the environment and as a result the water surface become cooler. The heat loss from the water surface and accompany by the heat adsorbed by the surroundings will continue until the equilibrium temperature distribution is reached. The temperature of the water surface is highly increased with adsorption of the monolayer that resistance against evaporation (Jarvin et al., 1962). With a monolayer with high resistance to evaporation, the net result of reduction of evaporation by the adsorption of monolayer at water surface and the increase of temperature (which normally increases the rate of evaporation) will significantly decrease the loss of water through evaporation. On the other hand, the molecular structure of the monomolecular films also plays a major role in determining the effectiveness of retardation of evaporation process (Jarvin et al., 1962). Previous works have found out that any variation in molecular structure that prevented the formation of close-packing of the hydrocarbon chain such as the present of unsaturated or ionized polar groups (e.g. octadecyl amine on the stearic acid) which acts

as monomolecular film exhibits no resistance against evaporation. Also, the replacement of an aliphatic hydrogen atom for a larger substituent, such as halogens or hydroxyl group will decrease the ability of the monolayer to retard water evaporation. From previous findings, the factors that determine the best monomolecular film for evaporation resistance of water will be more related to intermolecular cohesion, for example the length of hydrocarbon tail rather than the nature of the polar hydrophilic head of the substances. Higher concentration of monolayer thickness of liquid surface will reduce the evaporation rate of the liquids.

- **Intermolecular interference on the surface of a liquid** - When there is more energy available to the molecules, the faster they will move around in zig-zag paths by means of Brownian motion. As a result, the probability that the molecules will bump into each other will be increased. This reaction triggers a "chain reaction", in which the collision between molecules continues until all molecules are moving. When the collision between two molecules occurs at the right angle and with enough energy, one molecule will be ejected from the surface of the liquid (Jozsef, 2009). The ejected molecule will combine with the previous ejected ones and known as evaporated substances. Thus, the higher the collision rate between liquid molecules will increase the evaporation process.
- **Stirring effect**- When the liquid is stirred, the molecules form the bulk liquid will have a chance be brought to the liquid surface. By having enough kinetic energy, the molecules may escape from the surface.

### 1.2.2 Method of measuring evaporation rate

There are two main categories of measuring evaporation rate of organic compounds as reported by previous studies (Gavril et al., 2006). It involved the measurement of weight gain of vapor adsorbent above the liquid surface (Dilling et al., 1975; Mackay and Leinonen, 1975; Mackay and Wolkolf, 1973) and the measurement of the rate of liquid

loss into the moving gas stream that flowing horizontally above the liquid surface (Beverley et al., 1999; Rusdi and Moroi, 2004). The former allows the measurement of evaporation rates across a stagnant gas phase while the latter measures the evaporation rates in perturbation gas flow. Most of the methods only measure the relative evaporation rates and evaporation halftimes which may not portray the real physical phenomena.

For this work, the evaporation rate of alcohol in the alcohol-water mixtures at different concentration and the influence of surfactants are measured using Reversed-Flow Gas Chromatography (RF-GC). Most of the previous work measured the rate of evaporation of alcohol and diffusion coefficients separately (Fuller et al., 1969; Fuller et al., 1965, 1966; Grushka and Maynard, 1972; Hangrove and Sawyer, 1967). RF-GC is used in the work since the system RF-GC allows the two physicochemical measurement to be done simultaneously (Karaiskakis and Gavril, 2004; Karaiskakis and Katsanos, 1984).

### 1.2.3 Diffusion Coefficient

In order for us to understand the diffusion process, molecular approach is needed to understand the molecules in motion. The next discussion will be focused on the time–dependent diffusional process. The process involves the spreading of molecules with time. Example of this phenomenon is the concentration distribution in a solvent to which a solute was added. The aim of the next discussion is to obtain an equation for the rate of change of the concentration of particles in an inhomogeneous region.

The underlying rules that govern the momentum transport will be the Newton's law of viscosity while the energy transport will involve the Fourier's law of heat conduction. The principle rules governing the mass transport are the Laws of Fick (Bird et al., 2002). The first of this laws states that the flux of matter (the number of particles passing through an imaginary window in a given interval divided by the area of the window and the duration of the interval) is proportional to the density gradient at that point. Based on the experimental observation of transport properties (Figure 1.2), it is shown that the flux of a property is usually proportional to the first derivative of some other related property (in this case, the number density of particles). Thus, the flux of matter diffusing (say parallel to z-axis) in a close rectangular box will be proportional to the first derivative of the concentration:

$$J(matter) \propto \frac{dN}{dz} \tag{1.7}$$

where $N$ is the number density of particles with units number per meter cubic ($m^{-3}$) and $J$ are numbers per meter squared per second ($m^{-2}\ s^{-1}$).

The First Fick's law implies that if the concentration varies steeply with position, then diffusion will be fast. On the other hand, if the concentration is uniform throughout the system, then there no net flux, i.e. $\frac{dN}{dz} = 0$. Based on the Figure 1.2, a positive value

of *J* reflects a flux towards the positive value of z-axis while a negative value of J means a flux towards the negative value of z-axis. Since the molecules flow down a concentration gradient, i.e. from high concentration towards low concentration, thus *J* value will be positive and $\frac{dN}{dz}$ will be negative.

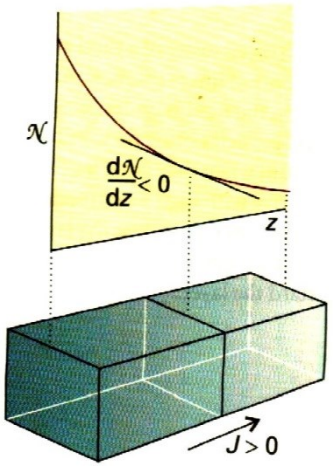



**Figure 1.2:** The flux of particles down a concentration gradient (see the concentration of the grey color inside the box decreasing from left to the right). Fick's law states that the flux of matter (the number of particles passing through imaginary window in a given interval divided by the area of the window and the duration of the interval) is proportional to the density gradient at that point (Atkins and Paula, 2006)

Thus, the coefficient of proportionality in equation (1.7) will be negative, -*D*;

$$J(matter) = -D\frac{dN}{dz} \tag{1.8}$$

Then, if both sides of Equation (1.8) is divided by Avogadro's constant, then we will convert the unit from numbers into amounts (numbers of moles);

$$J = -D\frac{dc}{dz} \tag{1.9}$$

where *D* is the diffusion coefficient ($cm^2/s$), $\frac{dc}{dz}$ is the concentration gradient along z-axis and *J* is the number of moles of molecules passing through a unit area in a particular interval of time. Equation (1.9) is usually applied to molecular diffusion. The equation is

also applicable in a great variety of natural transport phenomena such as the horizontal flow of water in unsaturated soils, the mixing of air masses in the atmosphere, the penetration of light into clouds or snow, the flux of neutron in pile and etc. (Giddings, 1965).

Considering a thin slab (the molecules enter the slab via the *green* entrance and left the slab via the *yellow* entrance) of a cross section, $A$ that extends from $x$ to $x+l$ as shown in Figure 1.3:

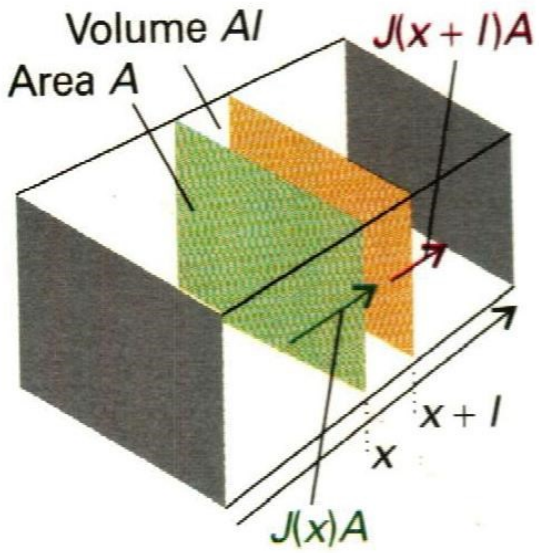



**Figure 1.3:** The net flux in a region is the difference between the flux entering from the region of high concentration (on the left) and the flux leaving to the region of low concentration (on the right) (Atkins and Paula, 2006)

The amount (number of moles) of molecules that enter the slab in the infinitesimal interval d$t$ is $JA$d$t$. The rate of increase of molar concentration inside the slab (with volume $Al$) which result from the flux of the molecules that enter the slab from *green* entrance is

$$\frac{\partial y}{\partial x} = \frac{JAdt}{Aldt} = \frac{J}{l} \tag{1.10}$$

There is also an outflow of the molecules via the *yellow* entrance. The flux that pass through the *yellow* entrance, and the rate of change of concentration that result is

$$\frac{\partial c}{\partial t} = -\frac{J'Adt}{Aldt} = -\frac{J'}{l}$$

(1.11)

The net rate of change of concentration is

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

(1.12)

Each flux will be proportional to the concentration gradient at the entrance. Thus by using the Fick's first law (Equation (1.8)), we can write

$$J - J' = -D\frac{\partial c}{\partial x} + D\frac{\partial c}{\partial x} = -D\frac{\partial c}{\partial x} + D\frac{\partial}{\partial x}\left\{c + \left(\frac{\partial c}{\partial x}\right)l\right\} = Dl\frac{\partial^2 c}{\partial x^2}$$

(1.63)

Or

$$J - J' = Dl\frac{\partial^2 c}{\partial x^2}$$

(1.14)

By dividing both sides of Equation (1.14) with *l*, we will get

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l} = D\frac{\partial^2 c}{\partial x^2}$$

(1.15)

which also known as Fick's second law of diffusion which relates the rate of change of concentration at a point to the spatial variation of the concentration at that point (Atkins and Paula, 2006). Equation (1.15) also describes the concentration profile that evolve with time.

Diffusion coefficient is a constant between the molar flux due to molecular diffusion and the gradient in the concentration of the species. Diffusion coefficient is a physical constant dependent on molecule size and other properties of the diffusion substance as

well as on temperature and pressure. Diffusion coefficient, also called Diffusivity, is an important parameter indicative of the diffusion mobility. Diffusion coefficient is generally prescribed for a given pair of species. For a multi-component system, it is prescribed for each pair of species in the system. The higher the diffusion coefficient (of one substance with respect to another), the faster they diffuse into each other. Therefore, this parameter can be an important parameter to describe the transport of pollutant gases in the air (Spagnolo and Barerra, 2002). Diffusion coefficient also has been used to represent the average spread of emissions (Cheng et al., 2011).

### 1.2.4 Measurement of Diffusion Coefficient

Various methods have been developed for the measurement of diffusion coefficient (Karaiskakis and Gavril, 2004). These methods are mainly based on gas chromatography techniques which include stopped-flow gas chromatography (Katsanos et al., 1981; Phillips et al., 1967; Stolyarov and Kartsova, 1987), gas chromatography broadening technique based on mass balance and Golay equations (Maynard and Grushka, 1975), continuous elution method (Giddings, 1965; Giddings and Seager, 1960; Giddings and Seager, 1961; Giddings and Seager, 1962) and arrested elution method (Knox and McLaren, 1963, 1964). Mathematical correlation for the prediction of diffusion coefficients also has been reported. In this study, RFGC was used to measure the diffusion coefficients of alcohol in the alcohol-water mixtures at different concentration. Previous studies showed that RFGC has been successfully used for the determination of diffusion coefficient of various pure liquids such as methanol, ethanol, 1-propanol, n-pentane, n-hexane, n-heptane and n-hexadecane (Karaiskakis and Katsanos, 1984; Katsanos, 1988; Khalid et al., 2012).

#### 1.2.4.1 Stopped-Flow Gas-Chromatography technique

Stopped-Flow GC was introduced by Philips and his co-workers (1967) to study the kinetics of surface catalyst reactions. The Figure 1.4 shows the experimental setup of stopped-flow GC for measuring gas diffusion coefficients. Stop-Flow GC methodology is based on stopping the flow of the carrier gas in very short time interval (Karaiskakis et al., 1986). FID is being used as detector for this experiment and both column *L* and *l* are empty columns (Figure 1.4). For measurement, small amount of solute is injected into the diffusion column, *L* as the carrier gas is continuously flowing through column *l*. The flow of the carrier gas is stopped for a particular time by closing the valve $V_1$ and $V_2$ from the

moment of injection. Narrow peak (stop peak) is produced after each time the gas flow is restored as depicted in Figure 1.5:

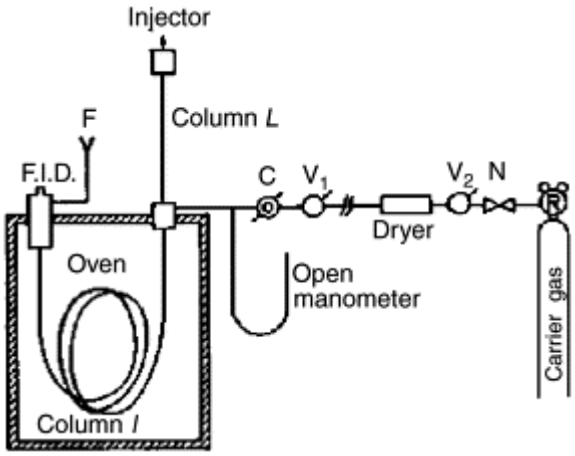



**Figure 1.4:** Stopped-flow chromatography for determining diffusion coefficients. N: needle valve, $V_1$, $V_2$: shut-off valves for stopping and restoring carrier gas flow through column *l*, C: gas flow controller, F: bubble flow meter (Karaiskakis and Gavril, 2004)

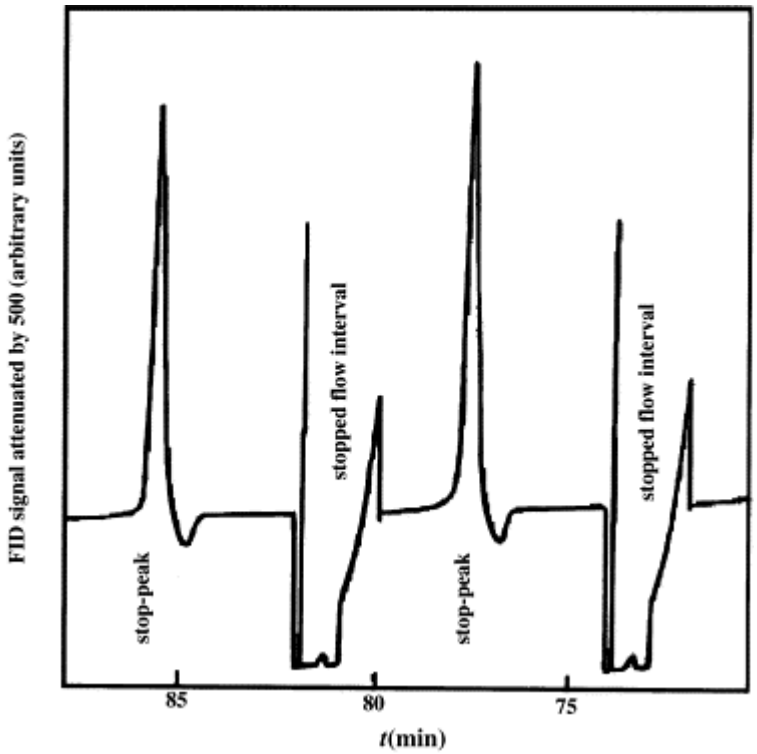



**Figure 1.5:** Stopped-flow chromatogram for measuring diffusion coefficients (Karaiskakis and Gavril, 2004).

Below are the assumptions that were drawn for stopped-flow GC method:

- Radial diffusion in the column was negligible.

- Axial diffusion in the chromatographic column *l* was negligible.
- Solute was introduced in an "infinitesimally" small section of the diffusion column, *L*, and the band can be described by a delta function, δ.

The equation below was used by Katsanos et al. (1981) when the Stop-Flow GC was used to determine the diffusion coefficient of solute gas into the carrier gas which was nitrogen:

$$\ln\left(ht^{\frac{3}{2}}\right) = \ln\left(\frac{mt_sL}{\pi^{\frac{1}{2}}D^{\frac{1}{2}}}\right) - \frac{L^2}{4D}.\frac{1}{t} \tag{1.16}$$

where, *h* is the height from the base line of stop-peak, *t* is the time interval from injection of solute gas to the beginning of stopped-flow interval(s), *m* is mass of injected solute gas (mol), $t_s$ is the stopped-flow interval time(s) and *L* is the length of diffusion column in cm.

The diffusion coefficient, *D* was calculated from the slope($-\frac{L^2}{4D}$) of the graph $\ln(ht^{\frac{3}{2}})$versus $\frac{1}{t}$. The diffusion coefficient, *D* does not differ significantly when the length of the diffusion column, *L*, length of the chromatographic column, *l*, or the volume of the carrier gas is varied as reported by Katsanos et al. (1981). The results just varied within 95% fiducially limit of the mean values when the mentioned parameters were varied

### 1.2.4.2 Gas Chromatography broadening techniques

Determination of diffusion coefficients by gas-chromatography broadening technique was first introduced by Giddings and Seager (1960) and has been used by many other workers as originally created by Giddings and in several modified form (Maynard and Grushka, 1975). The most basic setup of the experiment includes a commercial GC where the packed column being replaced with a coiled, long, empty tube of circular cross section as shown in Figure 1.6:

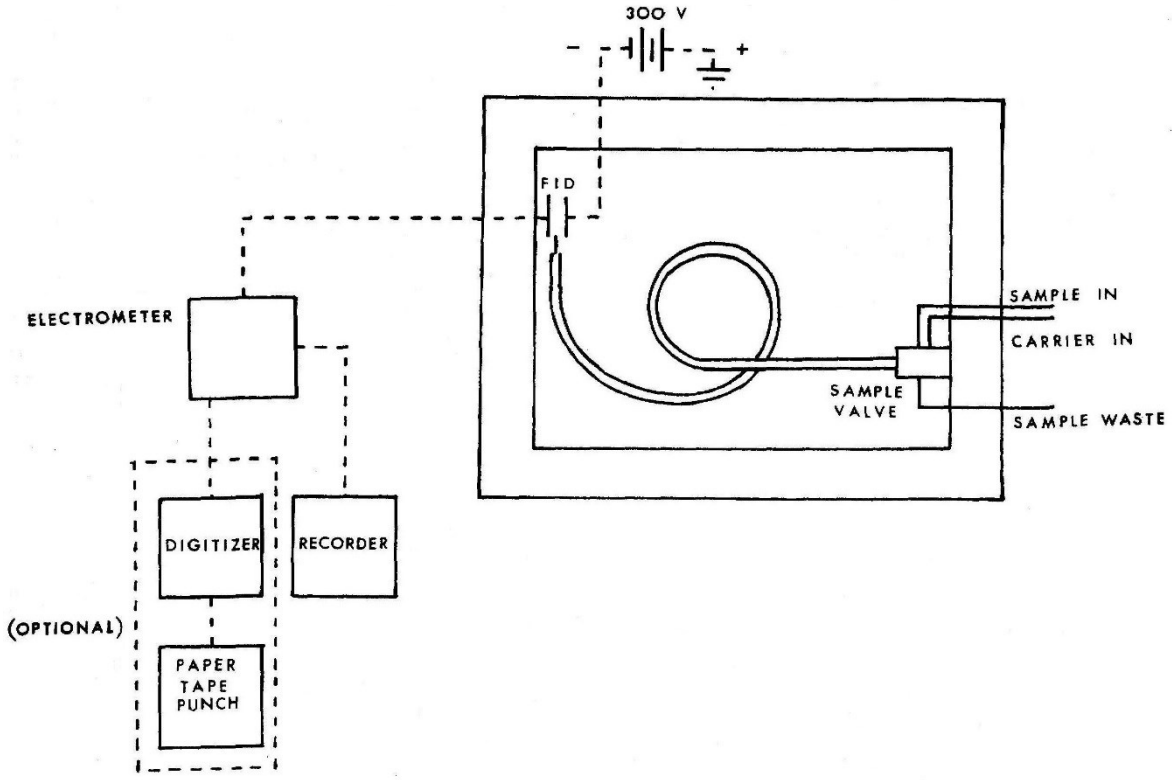



**Figure 1.6:** Basic apparatus for measuring diffusion coefficients by gas chromatography (Maynard and Grushka, 1975)

Liquid sample under study was injected into the sample valve with microliter syringe through the "sample in" opening (Figure 1.6). Inside the sample valve, the liquid will be heated at certain temperature until the liquid transform into the vapor. The vapor sample will be carried throughout the column to detector, FID by the carrier gas. The liquid

sample which was not transform into the vapor will be eluted out from sample valve as sample waste. Then the signal from the FID will be transformed into broadening peak sample (Figure 1.7) by electrometer and recorded or digitized on a paper.

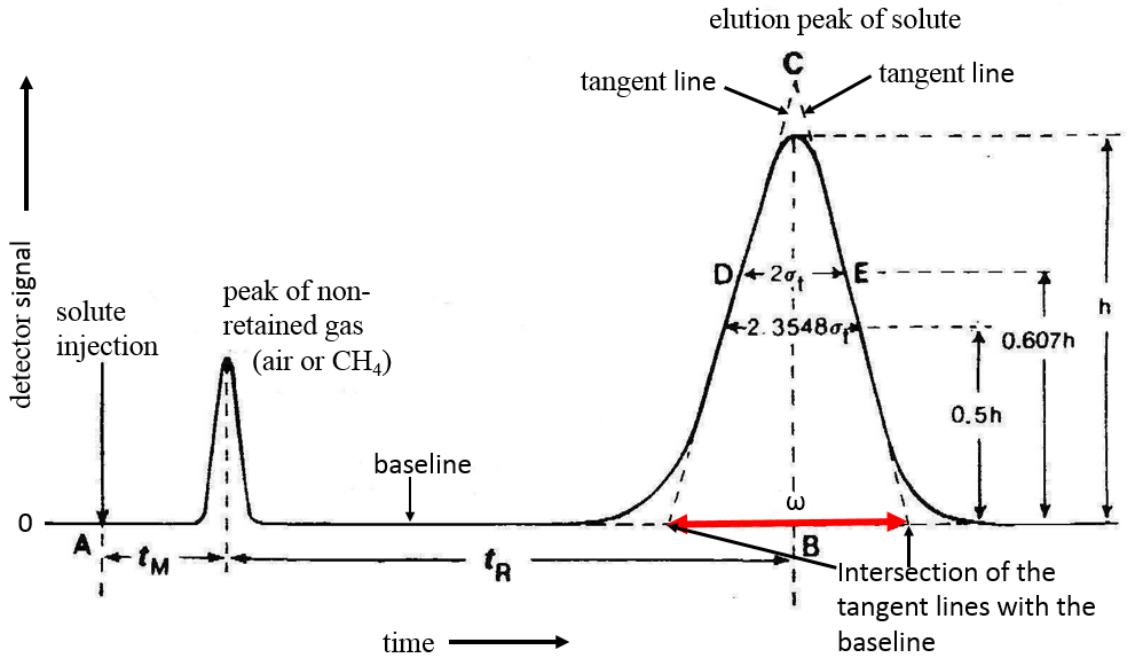



**Figure 1.7:** Typical appearance of an elution chromatogram after the injection of a single solute (Katsanos, 1988). $t_m$ = hold-up time/dead time, $t_R$ = retention time, $\sigma_l$= standard deviation in length unit, $h$ = height

The information obtained from an elution chromatogram consisted of Gaussian-type sample peaks, the time for diffusion, and the carrier gas flow rate. Tangents were drawn at the inflection points of each peak and extended to the baseline. The distance between the intersections of these tangents with the baseline was taken as the peak width at the baseline, ω.

GC broadening techniques require two main equation as pillar of its theoretical part:

- Mass-balance equation
- Golay equation

The selection of the equation was based on the type of the column being used, i.e. uncoated open tube column or coated open tube column (Maynard and Grushka, 1975). Mass balance equation was used to determine the measurement of diffusion coefficient of a solute into carrier gas in the open tube column whereas Golay equation was used if the diffusion coefficient measurements were carried out in the coated open tube.

**Mass-balance equation**

The diffusion in flowing fluids was first studied by Taylor (1953, 1954a, 1954b) and Aris (1956). Based on their findings, the diffusion of a solute in an open tube containing a flowing solvent can be explained by using a mass-balance approach. The diffusion of a solute in an open tube containing a flowing solvent can be described by mass-balance equation as follows:

$$\frac{\delta c}{\delta t} - D_{AB}\left[\frac{\delta^2 c}{\delta x^2} + \frac{1}{r}.\frac{\delta}{\delta r}\left(r\frac{\delta c}{\delta r}\right)\right] + 2\overline{U}\left[\left(1-\frac{r}{r_0}\right)\right]^2\frac{\delta c}{\delta x} = 0 \qquad (1.17)$$

where, $c$ is the concentration, $t$is the time, $D_{AB}$ is the binary diffusion coefficient of the solute-solvent pair, $x$ is the longitudinal coordinate of the tube, $r$ is the radial coordinate of the tube, $\overline{U}$ is the average solvent (carrier gas) velocity and $r$ is the radius of the tube. Equation 1.17 was based on the following assumptions:

a. No solute passes through the tubing wall.
b. The radial concentration gradient is zero, i.e. $\left(\frac{\delta c}{\delta r}\right)_{r=0} = 0$ at midpoint of the tube.
c. The solute that being introduced into the tube is assumed to be a delta function, δ.
d. Small ratio between the solute wall collisions to solute-solvent collision.

e. Turbulence is not present since the flow is laminar.

The Equation 1.17 can be solved by correlating with plate height, *H*:

$$H = \frac{2D_{AB}}{\overline{U}} + \frac{r_0^2 \overline{U}}{24D_{AB}} \tag{1.18}$$

**Golay Equation**

Beside the mass-balance equation, the Golay equation also has been used to describe the band broadening in the coated open-tube column:

$$H = \frac{2D_{AB}}{\overline{U}} + \frac{2R(1-R)}{3} \cdot \frac{d_f^2 \overline{U}}{D_L} + \frac{(11 - 16R + 6R^2) r_0^2 \overline{U}}{24D_{AB}} \tag{1.19}$$

where, $R$ is the ratio of solute velocity $d_f$ is the thickness of the stationary-phase film coated on the tube and $D_L$ is the diffusion coefficient of the solute in the stationary phase. The Golay equation can be reduced to Equation 1.19 when $d_f = 0$ and when there is no retention of the solute, i.e. $R = 1$. Below is the result of the rearrangement of Equation 1.19:

$$D_{AB} = \frac{\overline{U}}{4}\left[H \pm \left(H^2 - \frac{r_0^2}{3}\right)^{\frac{1}{2}}\right] \tag{1.20}$$

Only one value of the diffusion coefficient obtained from Equation 1.20 is meaningful. The diffusion coefficient, $D_{AB}$ can be determined from the positive square root because the second term on the right hand side of equation 1.20 is small when the velocity is slow. At high velocities, the negative square root was used instead of the first term in equation 1.20. By differentiating equation 1.20 with respect to $\overline{U}$ and leaving the equation equal to zero, the minimum value of $H$ (by optimizing the velocity, i.e.$\overline{U}_{opt}$) was obtained (Equation 1.21).

$$\overline{U}_{opt} = \frac{(48D_{AB})^{\frac{1}{2}}}{r_0}$$

(1.21)

### 1.2.4.3 Continuous elution method

The experiment of diffusion coefficient ($D_{AB}$) determination by using continuous elution procedure used an open tube with circular cross section (Karaiskakis and Gavril, 2004) in a commercial GC apparatus. The average carrier gas velocity, $\overline{U}_{opt}$ was chosen to minimize the plate height, *H*. Instead of the benefit of short analysis time, the disadvantage of this method is an inadequate zone broadening factors. In this method, all experimental data were obtained by using the short and the long column which was used to solve the end effects for diffusing that occurred in the instrument dead volumes (Karaiskakis and Gavril, 2004). The *H* value is obtained from the following equation:

$$H = (L_d - L_c).\left[\frac{\tau_d^2 - \tau_c^2}{(t_d - t_c)^2}\right]$$

(1.22)

where, $L_d$is the length of the long column, $L_c$ is the length of the short column, $\tau_d^2 - \tau_c^2$ is the difference for the second of the time base and $t_d - t_c$ is the difference for the first moment of the time base. τ was determined for the sample peaks as ω/4, where ω is the peak wide at the baseline (Figure 1.7).

### 1.2.4.4 Arrested elution method

In the arrested elution method, the diffusion coefficients, $D_{AB}$ and obstructive factor, $\gamma$ were determined by using an empty column and a packed column, respectively (Knox and McLaren, 1964). The experimental setup for the method is shows in Figure 1.8

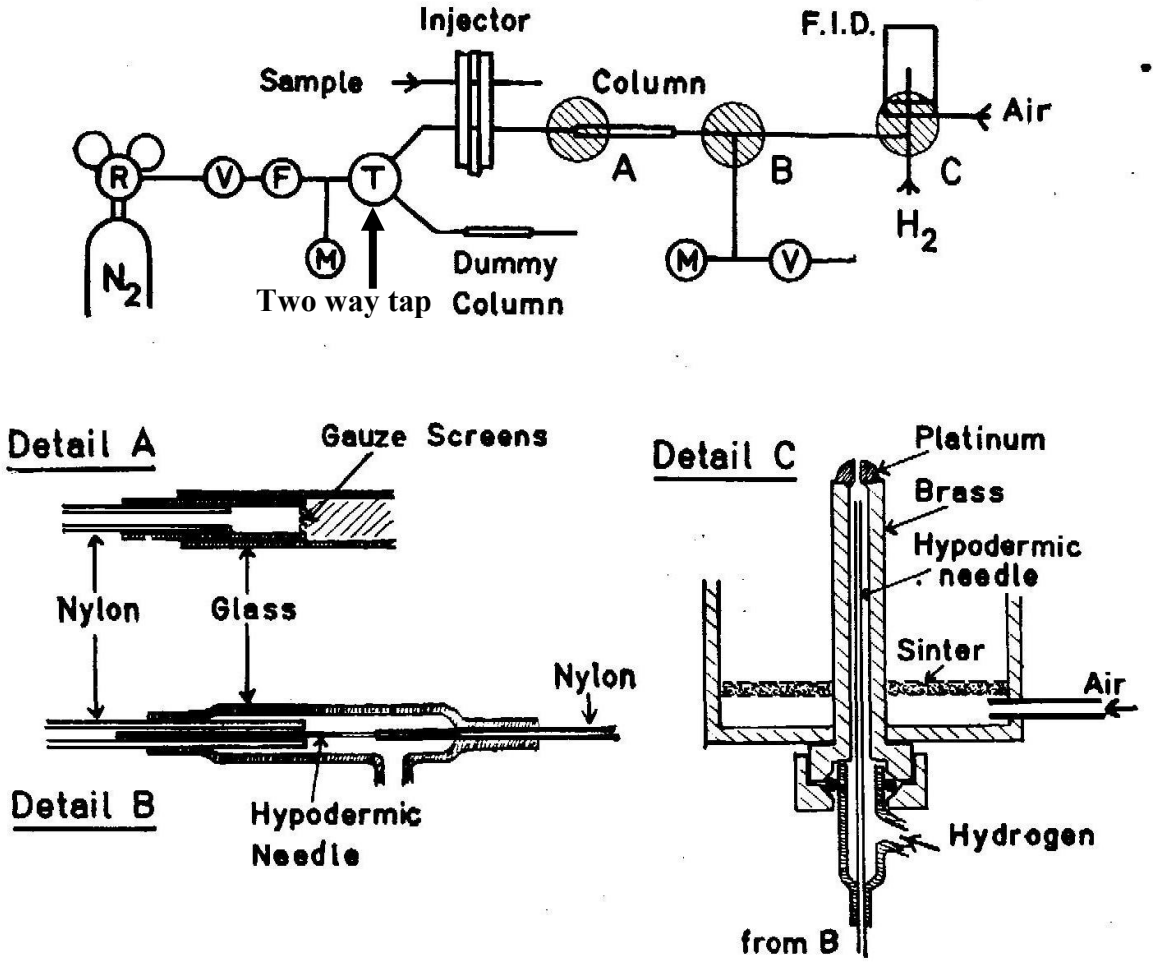



**Figure 1.8:** Gas line and details of important connections for arrested elution method. (Knox and McLaren, 1964). *R* = two-stage reducing valve and pressure regulator, *V* = needle valve, *F* = flow meter, *M* =manometer, *T* = two-way tap, F.I.D. = flame ionization detector, A, B, and C refer to detailed connection shown in lower part of Figure 1.8

The experimental procedure for this method is as follow: Firstly, the solute sample was injected into the column and the carrier gas was eluted in the normal way without arresting the flow of the carrier gas. This action will enable the calculation of the time of passage along the column of the sample which calculated from the total time elapsing

between injection and detection and from the volumes of the column. The velocity of the sample carried by the carrier gas at the outlet was obtained by using the time of passage along the column. For the static spreading study in a particular column, the sample gas was allowed to elute half way along the column at the constant flow rate as in the continuous elution experiment. Then, the flow of the sample gas was switched to a Dummy Column of equal resistance (Figure 1.8). This was done by turning the two way tap, *T* placed at upstream of the injector (Figure 1.8). The flow then reconnected after 1 to 20 minutes and resulting in the elution of the peak. The spreading of the band can only occur during the delay time by diffusion. Finally, the band is eluted at known concentration profile and velocity from the column while the standard deviation is determined by the gas chromatography detector. The additional variance, $\sigma^2$ produced by diffusion during the delay period is obtained:

$$\frac{d\sigma^2}{dt} = \frac{2D_{AB}}{\bar{u}^2} \qquad \text{(empty tube)} \tag{1.23}$$

$$\frac{d\sigma^2}{dt} = \frac{2\gamma D_{AB}}{\bar{u}^2} \qquad \text{(packed tube)} \tag{1.24}$$

Regardless of the delay, the band broadening resulted from the injector, column connections, detector and elution along the column was identical. A linear line was obtained from a plot of $\sigma^2$ against delay time with the gradient of $\frac{2D_{AB}}{\bar{u}^2}$ and $\frac{2\gamma D_{AB}}{\bar{u}^2}$ for empty and packed tube, respectively. $\bar{u}^2$ is the outlet elution velocity as shown in Axis-Y in Figure 1.9. The accurate measured of the outlet elution velocity, $\bar{u}^2$ is a must since it occur in the power of two and as denominator in the equation 1.23 and equation 1.24. The overall reproducibility of this methodology is ±2% (Knox and McLaren, 1964).

The method was reasonable since the pressure drop across the column during elution was low. On the other hand, larger pressure drop will curb the gas velocity and reaches a

constant value before the elution of the peak. In this case, the variance, $\sigma^2$ will be overvalued and resulting in a high value of diffusion coefficient.

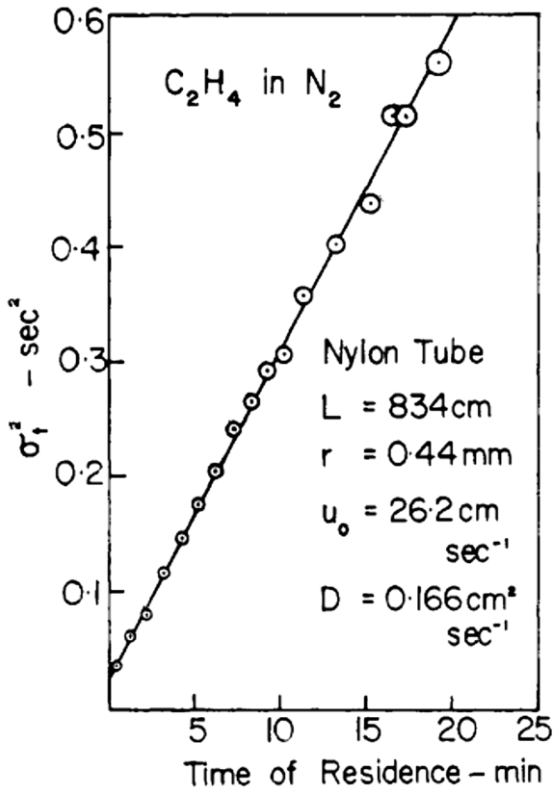



**Figure 1.9:** Change of variance with residence time by using empty nylon tube (Knox and McLaren, 1964)

The experimental data obtained from this work were intrinsically higher precision as compared to the methods based on *HETP* (Height Equivalent to the Theoretical Plate) measurements (Knox and McLaren, 1964). The open tube experiment was done by Knox and McLaren (1964) by using ethylene as the sample gas and nitrogen as the carrier gas. The experiment is conducted at constant temperature and pressure of 18 °C and 750 mm Hg, respectively. The diffusion coefficient obtained from this experiment was 0.165 sqcms$^{-1}$. On the other hand, when glass beads, firebrick and celite were used as packing materials for the packed column experiments and the values of $\gamma$ obtained were 0.60, 0.46 and 0.74, respectively. The standard deviation for both $D_{AB}$and $\gamma$ were about 2% for all columns by comparing the calculated and experimental values. The advantages of this work include the measurement was not affected by the effect of zone broadening that

contributed by the diffusion of other molecules and non-uniform flow profile. No assumption has been made about the accurate form of the flow profile, the smoothness of the column wall or the exact measurement of column diameter. However, the disadvantages of this method were the experiment needs to be conducted several times to produce high accuracy $D_{AB}$ value and the constant flow-rates need to be established over a long times period in order to allow the measurement at different arrested times (Karaiskakis and Gavril, 2004).

#### 1.2.4.5 Mathematical correlation in the prediction of binary gas system diffusion coefficients

The determination of the diffusion coefficient, $D_{AB}$, which have been discussed in the previous section produced variation in values. Thus, mathematical techniques have been developed and improved by several authors in order to make the $D_{AB}$ more accurate and reliable.

The limitation and accuracy of diffusion coefficient values mainly due to the fact that $D_{AB}$ which is inversely proportional to pressure, directly proportional to temperature and is almost independent of the composition for a given gas pair. The variations were deliberated and explained in different levels of accuracy by empirical equations of the kinetic theory of gases by Karaiskakis and Gavril (2004). Most of the empirical correlation mainly referred to the Stefan-Maxwell hard sphere model:

$$D_{AB} = \frac{a}{n\sigma_{AB}^2}\left[\frac{8kT}{\pi}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)\right]^{\frac{1}{2}} \tag{1.25}$$

where, $D_{AB}$ is the binary diffusion coefficient, $a$ is the constant with various values ($\frac{1}{3\pi}, \frac{1}{8}, \frac{1}{2\pi}$and $\frac{3}{32}$) depending on the nature of the experiment carried out by the researcher.

$n$ is the total concentration of both species, $T$ is the temperature, $k$ is the Boltzman constant, $M_A$ and $M_B$ are the molecular mass of solute (A) and carrier gas (B), and $\sigma_{AB}(= \frac{1}{2}(\sigma_A + \sigma_B))$ is the collision diameter. This can be justified by the Chapman-Enskong equation as shown below:

$$D_{AB} = \frac{0.00263T^{\frac{3}{2}}}{p\sigma_{AB}^2}\left(\frac{\frac{1}{M_A}+\frac{1}{M_B}}{2}\right)^{\frac{1}{2}} \tag{1.26}$$

where $p$ is the gas pressure in atm.

The limitations of equation 1.26 are as follow (Fuller et al., 1966):

- The 3/2 power temperature dependence values usually lie in the range 1.6 to 1.8.
- The difference between theory and experimental results mainly due to $\boldsymbol{\sigma}$ which decreases slowly with increasing temperature.
- Limitation of $\boldsymbol{\sigma}$ values available in the literature.
- The literature values of $\boldsymbol{\sigma}$ only available for small range of temperature since $\boldsymbol{\sigma}$ is temperature dependent.

The constraints of the hard sphere model were then improved by Arnold (1930) by introducing a Sutherland temperature correction into equation 1.26. As a result, this author successfully improved the temperature dependence by varying from $T^{\frac{3}{2}}$ to $T^{\frac{5}{2}}$. $\boldsymbol{\sigma}$ was estimated as the cube root of the sum of Le Bas atomic volume parameters. Thus, Arnold managed to solve the limitation of $\boldsymbol{\sigma}$ availability in the literature and opened the possibility in estimating the diffusion coefficients for any binary gas system (Fuller et al., 1966). In 1934, Gilliland (Giddings, 1965; Gilliland, 1934) has eliminated the Sutherland temperature correction instead of retaining the $\boldsymbol{\sigma}$ with molar volumes at boiling point estimated from the Le Bas parameters. The reason of this action is to increase the straight

forwardness since there was not much data for diffusion coefficients as a function of temperature to verify the Arnold correction. In 1950, Andrussow introduced $T^{1.78}$ (Andrussow, 1950; Giddings, 1965) while another researcher estimated $\boldsymbol{\sigma}$ from the cube root of the critical volume and this include Othmer and Chen (1966) that proposed 0.4 power of the critical volume. As the result, the second limitation of the hard sphere model was partially overcome by the correlations. The limitation was partially overcome because experimental values for critical volumes were only available for limited number of substances (Fuller et al., 1966). Othmer and Chen (1966) have provided a clearer approximation of the Hirschfelder-Bird-Spotz (HBS) equation by using the critical values of temperature ($T_c$) and volume ($V_c$) (Karaiskakis and Gavril, 2004). The equation of HBS is as shown below:

$$D_{AB} = \frac{0.00186T^{\frac{3}{2}}(\frac{1}{M_A}+\frac{1}{M_B})^{\frac{1}{2}}}{p\sigma_{AB}^2\Omega_{AB}} \tag{1.27}$$

where, $\Omega_{AB}$ is the collision integral depending on temperature and the interaction energy of the colliding molecule ($\mathcal{E}_{AB}$) (the values are in the function of reduced temperature $T^*= kT/\mathcal{E}_{AB}$ where $k$ is the Boltzman constant) and $p$ is the gas pressure in atm unit. The disadvantage of the HBS is that the evaluation of the $\boldsymbol{\sigma}_{AB}$ and $\Omega_{AB}$ that mainly obtained from viscosity measurements (Karaiskakis and Gavril, 2004). Othmer and Chen (1966) modified the HBS equation as follow:

$$D_{AB} = \frac{0.43(\frac{T}{100})^{1.81}(\frac{1}{M_A}+\frac{1}{M_B})^{\frac{1}{2}}}{p(\frac{T_{CA}T_{CB}}{10^4})^{0.1405}\left[(\frac{V_{CA}}{100})^{0.4}+(\frac{V_{CB}}{100})^{0.4}\right]^2} \tag{1.28}$$

However, an important consideration should be taken into account in estimating diffusion coefficients with high precision by using equation 1.28 is that more complicated methods need to be derived from the HBS equation. This methods need a detailed gas dynamics

and thus only applicable for unusual system like large molecules or high temperature where the equations of Gilliland (equation 1.29) and Arnold (equation 1.30) has been not tested for such systems (Karaiskakis and Gavril, 2004).

$$D_{AB} = \frac{0.0043T^{\frac{3}{2}}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{P\left(V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}}\right)} \tag{1.29}$$

where $V_A$ and $V_B$ are molar volumes in cm$^3$ which can be obtained directly at the boiling points or by addition of the volume of molecular constituents.

$$D_{AB} = \frac{0.0083T^{\frac{3}{2}}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{p\left(V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}}\right)(1+\frac{c_{AB}}{T})} \tag{1.30}$$

where $c_{AB}$ is Sutherland's constant. Equation 1.30 introduces a second temperature term in the denominator which account for the molecular "softness". Thus, the temperature dependence in Equation 1.30 varying in the range $T^{\frac{3}{2}}$ (when the temperature at denominator, $T = 0$) to $T^{\frac{5}{2}}$ ($\frac{T^{\frac{3}{2}}}{\frac{1}{T}} = \frac{T^{\frac{3}{2}}}{T^{-1}} = T^{\frac{3}{2}+1} = T^{\frac{3}{2}}$).

The Fuller-Schettler-Giddings (FSG) equation on the other hand provides simplicity, reliability and accuracy in estimating the diffusion coefficients for gases. The FSG equation involves atomic and structural volume increments. Selected constants, i.e. temperature, $T$ and gas pressure, $p$ are able to vary freely. The correlation for the FSG equation has proven to be accurate since the data points are obtained from non-linear least square analysis which involve 340 values of the diffusion coefficients from the literatures

(Fuller et al., 1966). Fuller et al. (1966) stated that the FSG is just not simple to use but gave the high accuracy as compared to the other equations. The FSG equation is shown below:

$$D_{AB} = \frac{10^{-3}T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{p(V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}})^2} \tag{1.31}$$

where, $T$ is temperature, $M_A$ and $M_B$ are the molecular masses of solute A and carrier gas B, and $V_A$ and $V_B$ are special diffusion parameter (also known as diffusion volume) and $p$ is gas pressure in atm. Meanwhile, Huang et al. (1972) did the investigation on the effects of pressure and temperature on gas diffusivity and modified the Arnold equation (equation 1.30) as follow:

$$D_{AB} = \frac{5.06T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{p^{1.286}\left(V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}}\right)^2} \tag{1.32}$$

where, $V_A$ and $V_B$ are the molar volume, $T$ is temperature, $M_A$ and $M_B$ are the molecular masses of solute A and carrier gas B, and $p$ is gas pressure in atm. The accuracy of this method in the determination of diffusion coefficients was evaluated using 134 diffusion coefficients value from literature. Also the accuracy of other method was also calculated (Table 1.11).

**Table 1.1:** Average percentage accuracy of different methods tested for the prediction of binary gaseous diffusion coefficients for 134 literature $D_{AB}$ values (Huang et al., 1972).

| Method | Accuracy |
|---|---|
| Gilliland | 6.64 |
| Arnold | 11.75 |
| Hirschfelder-Bird-Spotz(HBS) | 18.99 |
| Chen-Othmer | 10.85 |
| Fuller-Shettler-Giddings (FSG) | 3.40 |
| Huang et al., 1972 | 3.52 |

### 1.2.4.6 Reversed Flow Gas Chromatography (RF-GC)

Previous works tend to measure evaporation rates and diffusion coefficient separately. By using the RF-GC methodologies, evaporation rates and diffusion coefficient can be determined simultaneously. The evaporation process which is explained in the previous section occurred at the lower end of the diffusion column of RF-GC. All the liquid molecules that escaped from the liquid surface are automatically diffused into the nitrogen gas which remains stagnant inside the diffusion column. The evaporated molecules are then transferred along the diffusion column and finally arrived at the other end of the diffusion column and then being carried to the detector by the moving nitrogen gas. This sampling procedure will produce the sample peaks. The sample peaks are then analyzed to calculate the evaporation rate and the diffusion coefficients of the liquid samples.

As indicated in previous section, Maynard and Grushka (1975) have reviewed the measurements of diffusion coefficients of a binary gas system by means of gas chromatography based on zone broadening technique. This method was based on the introduction of a small pulse of the solute gas into a long chromatographic column, in which the carrier gas is continuously flowing. This method resulted in the superposition of two different fluxes in the same direction and in one plane. The fluxes are diffusional flux, $-D\left(\frac{\partial C}{\partial x}\right)$, and "chromatographic" flux, $vc$ (where, $D$ is diffusion coefficient, $c$ is the concentration of solute vapor in the diffusion column, $x$ is distance coordinate and $v$ is linear velocity of the carrier gas in the chromatographic column). The simultaneously addition of those fluxes will result in two undesirable features. The performance of many separation processes depends on a series of equilibrium stages and is enhanced by providing more stages. Thus, a long chromatographic column is needed to increase the theoretical plates of the column (i.e. increasing the equilibrium stages inside the column).

As a result, the efficiency of the separation process (e.g. distillation, absorption, chromatographic, adsorption or etc.) will be increased as the number of theoretical plates increases (Green and Perry, 2007; Kiester, 1992). Since a long chromatographic column is needed for the diffusional flux to be manifested as the chromatographic signal, the precision of the method is relatively low (Karaiskakis, Lycourghiotis, et al., 1982). This problem could be improved if the two fluxes are separated by placing them perpendicular to each other (Karaiskakis, Katsanos, and Niotis, 1982a) as shown in the setup of RF-GC in Figure 1.10:

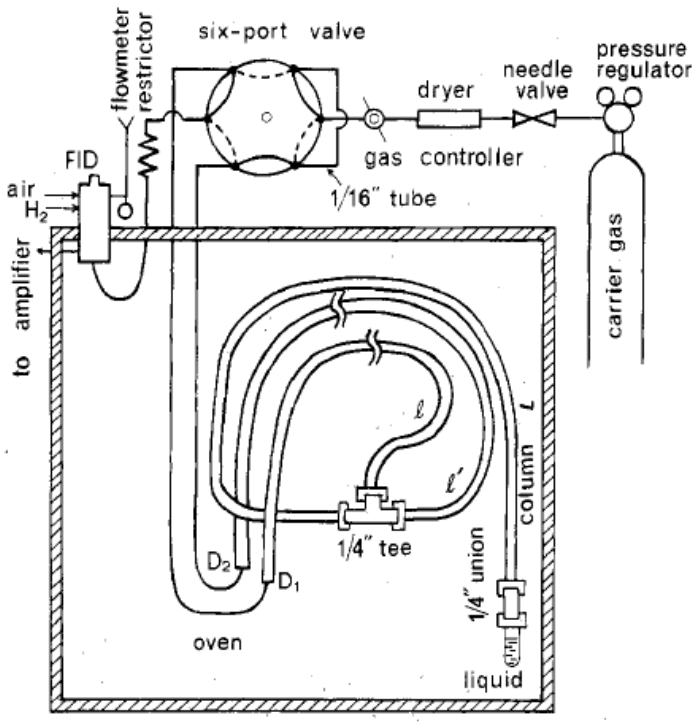



**Figure 1.10:** Instrumentation of the reversed-flow gas chromatography technique (Karaiskakis and Katsanos, 1984)

For RF-GC, the carrier gas will enter one end of the sampling column and enter the detector via the other end of the column. This process will make the carrier gas to be continuously flow through sampling column, either in forward or in reverse direction. However, the carrier gas will not flow through the diffusion column, but it remains stagnant in which solute gas is being introduced as liquid vapour (the liquid is being evaporated from small glass bottle at one end of the diffusion column).

A pure diffusion flux of the liquid sample into the carrier gas is occurred in the diffusion column and the result of this diffusional product at the junction between the sampling and the diffusion columns (1/4” tee) will be carried to the detector by the carrier gas as shown in Figure 1.11(a):

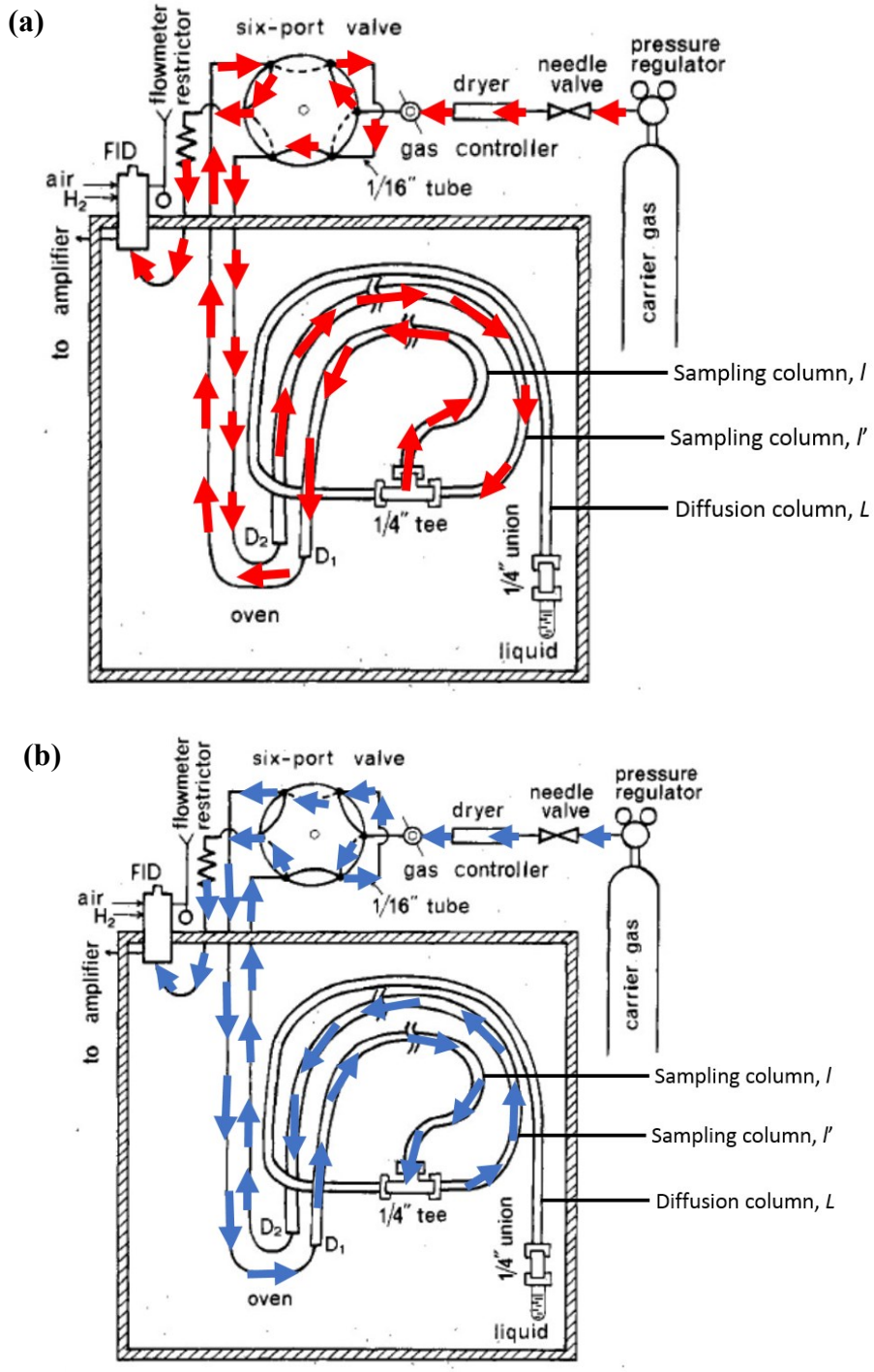



**Figure 1.11:** Instrumentation of the reversed-flow gas chromatography technique. *L* is the diffusion column while *l* and *l*' is the sampling columns. The movement of the carrier gas (in forward (a) and backward (b) directions respectively) is indicated by arrows. The carrier gas remains stationary in diffusion column, L (Karaiskakis and Katsanos, 1984)

Then, a concentration against time curve will appear as a signal for the product of the diffusional flux. The diffusion coefficient of the solute gas can be obtained from this curve. By repeating the sampling procedure and recording the amount of solute gas

entering the junction between the diffusion and the sampling columns, precise results within a small time interval can be obtained. The sampling procedure is accomplished by repeatedly reversing the direction of the carrier gas at definite known times in order to get the sample peaks (Figure 1.11b).

The advantage of this methodology as compared to the other gas chromatography methods of diffusion coefficients measurement is that the arrangement of the sampling and the diffusion columns is free from the "secondary flow" resulting from column that being coiled and to be placed inside the chromatograph oven (Karaiskakis, Katsanos, and Niotis, 1982a; Maynard and Grushka, 1975).

### 1.2.5 Application of RF-GC

The technique of reversed-flow gas chromatography (RF-GC) was first introduced by Prof. Katsanos and his co-workers at the Laboratory of Physical Chemistry, University of Patras, Athens, Greece (Agathonos and Karaiskakis, 1989a; Atta et al., 2002; Dalas et al., 1986; Gavril and Karaiskakis, 1999; Gavril, Katsanos, et al., 1999; Karaiskakis et al., 1983). This instrumentation has been used to determine the diffusion coefficients in binary (Katsanos and Karaiskakis, 1983) and in multicomponent (Karaiskakis et al., 1983) gas mixtures. The variation of diffusion coefficients with the temperature (Katsanos and Karaiskakis, 1982, 1983), adsorption equilibrium constant (Karaiskakis et al., 1982b) and the rate constants for removal of solvents from impregnated porous solids (Katsanos and Georgiadou, 1980) also has been carried out by using this instrumentation. This method also has been used to study the kinetics of a complicated reaction between two reactants in gas phase, namely the oxidation of carbon monoxide with oxygen with $CO_3O_4$ as catalyst. (Karaiskakis et al., 1983).

Many publications regarding to this technique have been published in renown international journals, these studies include the determination of catalytic conversion of reactants into products for various important surface catalyzed reactions (Karaiskakis, Katsanos, Georgiadou, et al., 1982; Katsanos et al., 1985; Kontinoupulus et al., 1982) and determination of Flory-Huggins interaction parameters and solubility parameters in polymer-solvent system (Agathonos and Karaiskakis, 1989b). Besides that, RF-GC also plays an important role in determination of rate of coefficients for evaporation of liquids (Karaiskakis and Katsanos, 1984), mass transfer and partition coefficients across gas-liquid and gas-solid interfaces (Katsanos et al., 1988; Katsanos and Dalas, 1987) and in the determination of adsorption energies, local monolayer capacities and local adsorption isotherms (Dremetsika et al., 2007; Gavril, 2002; Katsanos et al., 1999; Katsanos et al., 2001; Metaxa et al., 2007; Metaxa et al., 2009; Roubani-Kalantzopoulou, 2009). RF-GC

also has been used in determination of rate constant for sorption of various gases on bimetallic catalyst (Gavril and Karaiskakis, 1999; Gavril et al., 1999a, 1999b).

Recently, the application of this technique has captured significance attention from the researcher. This technique has been used for various physicochemical measurements, such as of rate coefficients and diffusion coefficients for the evaporation of organic solvents under the influence of surfactants (Atta et al., 2004) and mass transfer coefficients of gases into the liquids (Rashid et al., 2001). RF-GC has been used to study the evaporation of the pollutant liquids under the influences of the surfactant (Gavril et al., 2006; Mohammad et al., 2013) as well as the vigorous works from our laboratory which measured the diffusion rates, diffusion coefficients and activation energy (Khalid, 2011a, 2011b; Khalid et al., 2011a, 2011b, 2011c, 2011d, 2012) can be considered as the latest publication under this area. Furthermore, this methodologies also applied in separation for the growth phases of microbes (Lainioti et al., 2010), surfaces studies (Gavril, 2010; Metaxa et al., 2009), characterization of hybrid materials (Kołodziejek et al., 2013), characterization of polymeric coatings (Bakaoukas et al., 2013) and kinetic study of alcoholic fermentation (Lainioti and Karaiskakis, 2013).

## 1.3 Objective of study

Previous works have been intensively focused on the determination of the rate of evaporation of pure solvents such as alcohols and hydrocarbons (Karaiskakis and Katsanos, 1984; Khalid et al., 2011d). In this study, the rate of evaporation of alcohols from alcohol-water was study. So far, the rate of coefficient for evaporation of low molecular weight alcohol in water mixture has not been reported elsewhere.

The aim of the present work is:

- To determine the effect of water on the evaporation of alcohols from water-alcohol mixture.
- To study the influence of temperature, concentration of alcohol and carbon number on the evaporation of alcohols from water-alcohol mixture.
- To study the effect of surfactant concentration and the types of surfactant (nonionic, cationic and anionic surfactant) on the evaporation of selected alcohols.

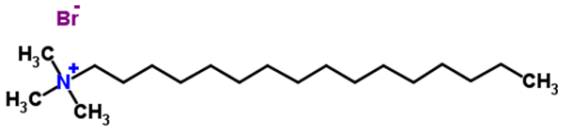
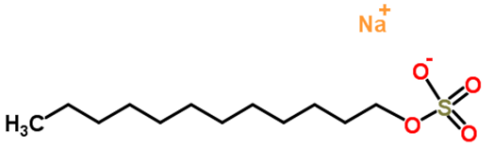
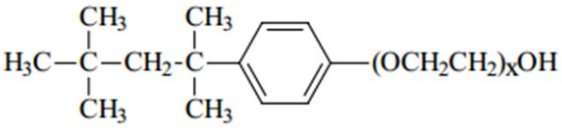
# CHAPTER 2

# EXPERIMENTAL

## 2.1 Chemicals

Methanol, ethanol, 1-propanol and 1-butanol were obtained from Merck (Germany). Nitrogen (99.999% purity), hydrogen and compressed air were purchased from Linde (Malaysia). Water used for all experiments was distilled water. The surfactants used in this study were cationic (hexadecyltrimetyl-ammonium bromide (CTAB)), anionic (sodium dodecyl sulfate (SDS)) and non-ionic surfactants (Triton X-100). The structure, molecular weight and abbreviation of these surfactants were listed in Table 2.1. CTAB and SDS were purchased from MERCK (Germany) whereas Triton X-100 (*iso*-octylphenoxypolyethoxyethanol) was purchased from Acros Organic (USA). All surfactants were used as received.

**Table 2.1:** The structures, molecular weight, density and abbreviations of surfactants used

| Surfactant | Abbreviation | Molecular weight ($gmol^{-1}$) | Density. *d* ($gmL^{-1}$) |
|---|---|---|---|
|  | CTAB | 364.45 | 1.402 |
|  | SDS | 288.372 | 1.01 |
|  x = 9-10 | TRITON X-100 | 646.37 | 1.06 |

## 2.2 Instrumentation

In this work, the apparatus set up and the experimental procedure were as described by previous studies (Karaiskakis and Katsanos (1984); Katsanos (1988)). The RF-GC used in this work was a modified conventional gas chromatograph (Shimadzu, Series GC-14B) equipped with flame ionization detector (FID) as shown in Figure 2.1 and Shimadzu Solution was used as the operating software. The GC system was connected to the computer via CBM-102 Communications Bus Module Shimadzu.

**Figure 2.1:** Modified Shimadzu GC-14B

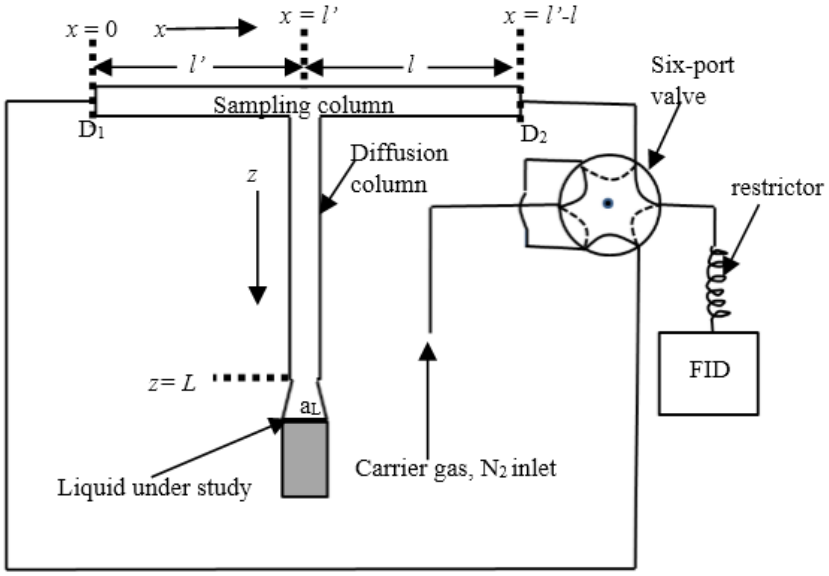



**Figure 2.2:** The set-up of RF-GC

**Figure 2.3:** Inner side view of chromatography oven

RF-GC is different from conventional gas chromatography where the conventional GC column was replaced with sampling and diffusion columns (Figure 2.2). The inner view of gas chromatography oven is shown in Figure 2.3. Diffusion column can be filled with liquid or solid or can be empty. In this study, the diffusion column was left empty for the diffusion coefficient measurements. The diffusion column (28.5 cm x

0.21 inch I.D.) was connected perpendicularly to the center of the sampling column *l'* and *l* with the length of 57 cm each and internal diameter of 0.21 inch. Both columns (*l'* and *l*) were connected by a 6.35 mm tee union (Swagelok). The empty columns used in this chromatography were stainless-steel tubing with 6.35 mm diameter. The carrier gas was set at 1 $cm^3min^{-1}$ with the continuously flow through the sampling column whereas the carrier gas was remained stagnant inside the diffusion column. A glass bottle (6 $cm^3$) filled with selected alcohol and alcohol water mixtures (4.0 $cm^3$) were connected at the lower close end of the diffusion column with a 6.35 mm Swagelok stainless steel nut.

A six-port valve as shown in Figure 2.2 was used to permit the carrier gas to enter either from $D_2$ and out at $D_1$ then immediately to the FID (valve position indicated by the solid line) or vice versa (the valve is switched to the dotted-line position). Through this valve, the flow of the carrier gas was reversed for short time interval and restoration to original direction. In this work, a high sensitive FID detector was selected. The main advantage of FID is the ability to possess a response factor of 1 (Equation 2.1).

$$Response\ Factor = \frac{Actual\ Concentration}{DataFID\ Response} \tag{2.1}$$

Therefore, FID will give a one to one response on whatever organic compounds that being burnt and ionized and manifested it into output (e.g. concentration-time curve). Furthermore, FID will not response to water (Karaiskakis et al., 1986; Katsanos and Dalas, 1987) and this will ensure that the exact amount of alcohol that diffused into the carrier gas will be measured. Table 2.2 summarized the RF-GC conditions used for the measurements in this study.

**Table 2.2:** The condition of Gas Chromatograph for the measurement of physico-chemical properties

| | |
|---|---|
| Detector Temperature | 475.15 K |
| Oven Temperature | 303.15 to 343.15 K |
| Diffusion column length | 28.5 cm (0.21 inch Internal Diameter, 0.25 inch Outer Diameter) |
| Sampling Column Length | 114 cm (0.21 inch Internal Diameter, 0.25 inch Outer Diameter) |
| Column Phase | Stainless steel (Purchased from Restek, Catalog No. 21515) |
| Carrier Gas Pressure | 101 kPa |
| Air Pressure | 190 kPa |
| Hydrogen Pressure | 150 kPa |
| Running Time | 140 Minutes |
| Reversal Time Interval | 6 Seconds |

## 2.3 Operation procedure for measurements

Before the measurement, every joint and connection in the system were checked for leakage with Swagelok Snoop leak detection liquid. Leakage of the system will be indicated by bubble formation at the joints or the connections of the system. When the RF-GC system was started, certain time was required for the baseline to stabilize. After the signal monotonously rising until the concentration-time curve for the vapor phase of the liquid was high enough, the chromatographic sampling procedure was started by reversing the direction of the carrier gas via the six-port valve. The valve was reversed for 6 s, a shorter time period than the gas's hold-up time in both columns $l'$ and $l$. The reversal process changed the initial direction of the carrier gas. After 6 s, the valve was reversed again and the direction of the carrier gas was returned to its original path. As a result, extra chromatographic peaks (sample peaks) were superimposed on the continuous elution curve as shown in Figure 2.4:

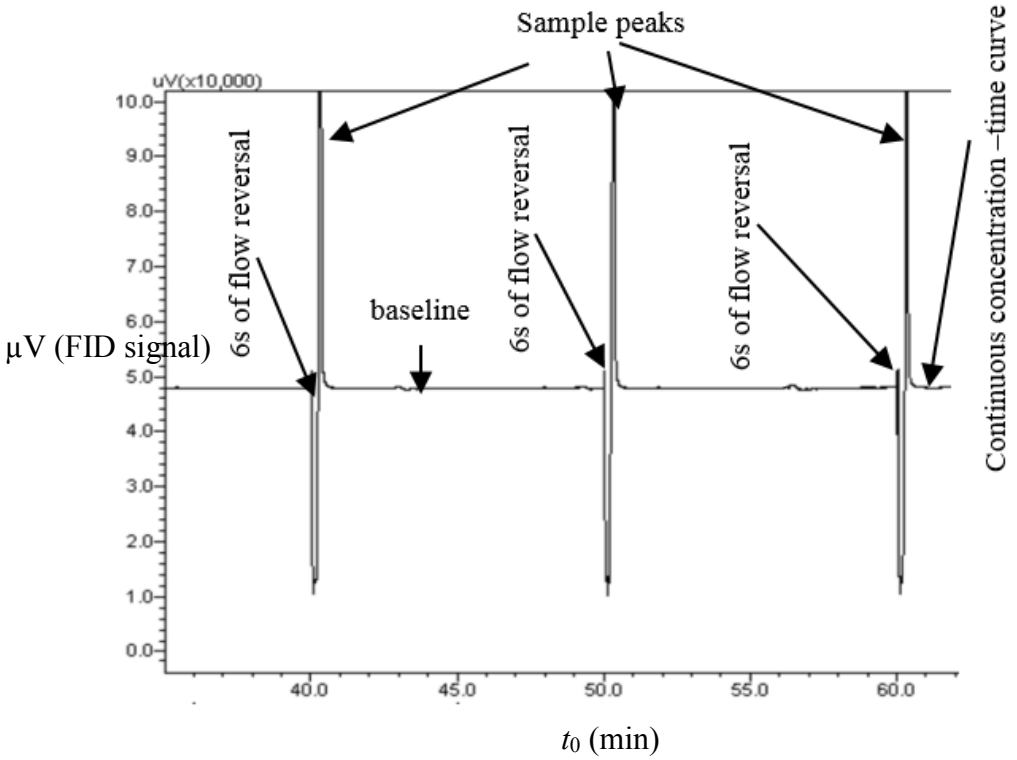



**Figure 2.4:** A reversed flow chromatogram showing two sample peaks for the diffusion of liquid particles into carrier gas nitrogen at 323.15 K and 101325 Pa (carrier gas flow rate = 1 $cm^3min^{-1}$), $t_0$ = Time from the beginning to the last reversal of gas flow

The process was repeated and lasted for 2 hours and 20 minutes. The pressure drop along section *l'* and *l* was negligible as the carrier gas flow rate was kept constant at 1.0 $cm^3s^{-1}$.

## 2.4 Theoretical basis

### 2.4.1 The chromatographic sampling equation

The methodology of RF-GC involved reversing the direction of the carrier gas flow from time to time. Thus, if the carrier gas was carrying other compound in gas phase, the trace of the latter can be recorded by FID. When the flow of the carrier gas was reversed, it will create perturbation on the chromatographic elution curve, having the form of extra "peak" sitting on the continuous concentration time curve as shown in Figure 2.5. Since the concentration of the flowing gas depends on the rate process which is taking place in the chromatographic column, then by reversing the flow, a sampling of this process can be performed.

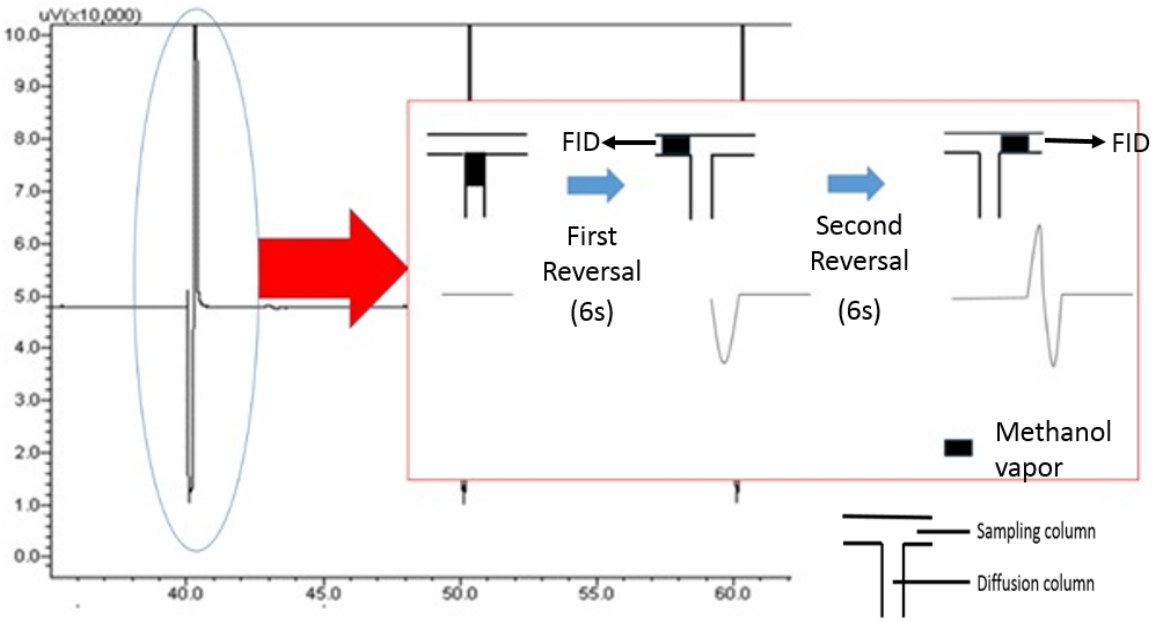



**Figure 2.5:** Sampling procedure by means of six-port valve

The rate process which influenced the concentration ($c$) is confined to a short section near the junction between the sampling column and the diffusion column as shown in the Figure 2.6:

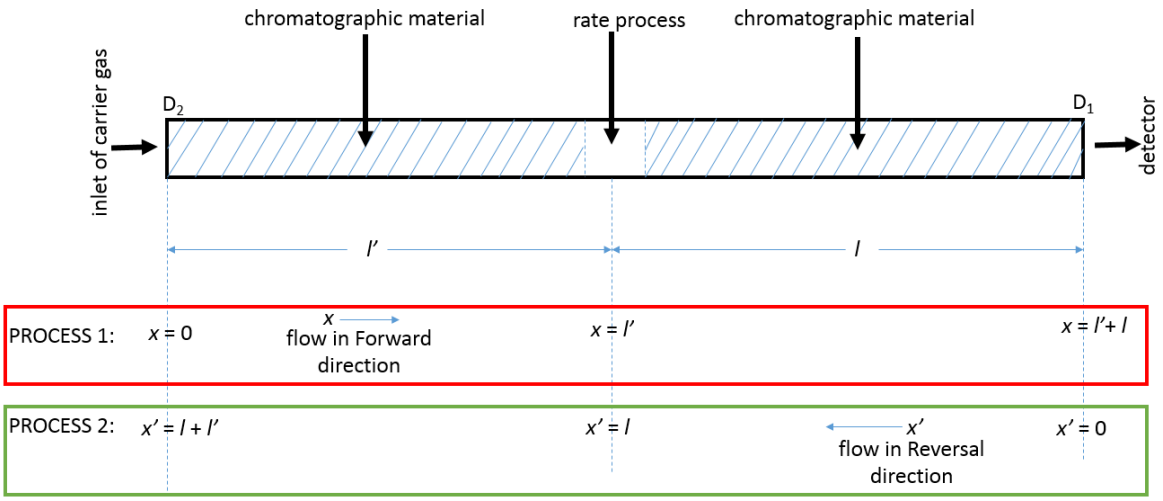



**Figure 2.6:** Rate process in the sampling column

A basic sampling procedure was derived with the following assumption (Katsanos, 1988):

- The adsorption isotherms of the carrier gas and the solute molecules in the sampling column were linear.
- *Axial diffusion* of the gases along the $x$ and $x$' axis in the sampling column and other phenomena leading to the non-ideality (e.g. mass transfer resistance in the stationary phase in the diffusion column, non-equivalent flow paths in the sampling column) were negligible. This can be assured with high carrier gas flow (Katsanos, 1988).
- The rate process was taking place in a sufficient short section of the sampling column. Thus, the contribution of solute gas concentration ($c$) along the $x$-axis can be described approximately by Direc delta function, $\delta(x - l')$.

The analysis was taken place separately for different time intervals. The concentration of solute gas was determined by certain equations as a function of time and distance (*x* or *x*)' given the initial and final states of boundary conditions. There are three types of time intervals:

1. During the original flow of carrier gas in the forward direction.
2. During the carrier gas which was carrying the solute gas flows in the interval of reverse direction.
3. During the carrier gas flows carrying the solute gas flow back into the initial direction.

The general mathematical equation describing the concentration-time curve of the sample peaks created by the flow reversals is described as follow (Katsanos, 1988; Katsanos et al., 1984):

$$c = c_1(l', t_0 + t' + \tau) \cdot u(\tau) + c_2(l', t_0 + t' - \tau) \cdot [1 - u(\tau - t')] \cdot [u(\tau) - u(\tau - t'_R)] + c_3(l', t_0 - t' + \tau) \cdot u(t_0 + \tau - t') \cdot \{u(t - t')[1 - u(\tau - t'_R)] - u(\tau - t')[u(\tau) - u(\tau - t'_R)]\} \quad (2.2)$$

where $t_0$ is the time measured from the beginning to the last backward reversal of gas flow, $t'$ is the time interval of backward flow of carrier gas, $t'_R$ is the time measured form the last restoration to the forward direction of the gas flow, $\tau = t - t_R$, $t$ and $t'_R$ are the retention times of the gas solute in the section lengths *l* and *l*' respectively and $u$ is the Heaviside unit step function. Heaviside step function or the unit step function, $u$ is a discontinuous function whose value is equal to zero for negative arguments and one for positive arguments. The function is used in the mathematical of control theory and signaling processing to represent a signal that switches on at a specified time and stays switched on indefinitely.

Equation 2.2 gives the concentration of gas solute at FID, as the sum of three terms, denoted by $c_1$, $c_2$ and $c_3$ (Figure 2.7). The terms are referred to the concentration of the gas solute at the junction of the diffusion and the sampling column $x = l'$ of Figure 2.2. Each of the concentration terms are then multiplied by a combination of Heaviside unit step functions. As a result, some terms are appear in a certain time interval and vanished in all others. Equation (2.2) predicts the sample peaks theoretically and its predictions coincide with the experimental sample peaks (c.f. Figure 2.7). The theoretical predicted peaks are square, whereas the actual sample peaks (Figure 2.8) were not square due to non-ideality (i.e. axial diffusion in column sections, *l* and *l'*) (Katsanos, 1988).

The height, *h* of the sample peaks above the continuous chromatographic signal (baseline) is proportional either one or two of the concentration terms, $c_1$, $c_2$ and $c_3$ of the Equation 2.2. For example of the sample peak of Figure 2.7, the maximum peak height is taken to correspond to its middle time, i.e. to $t = t_R + (t'/2)$ or $\tau = t'/2$.

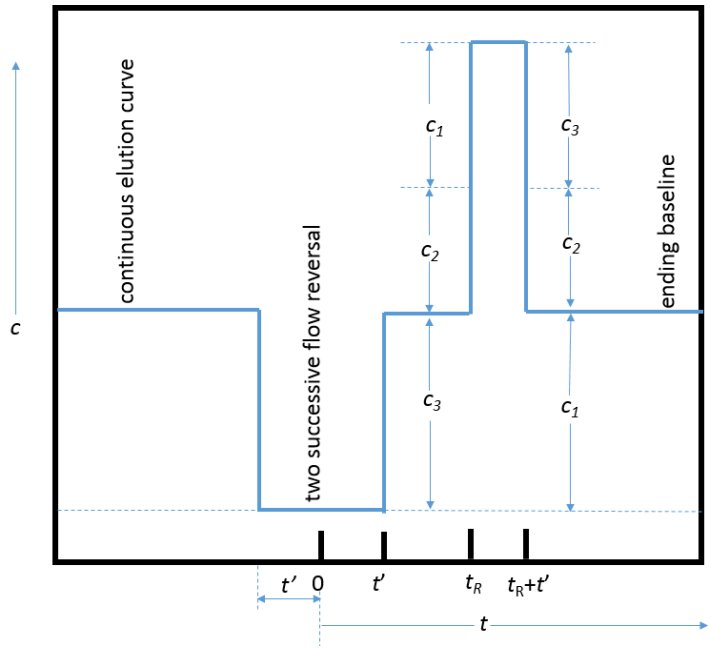



**Figure 2.7:** Elution curve predicted by Equation 3.2 when $t' < t_R$ and $t' < t'_R$

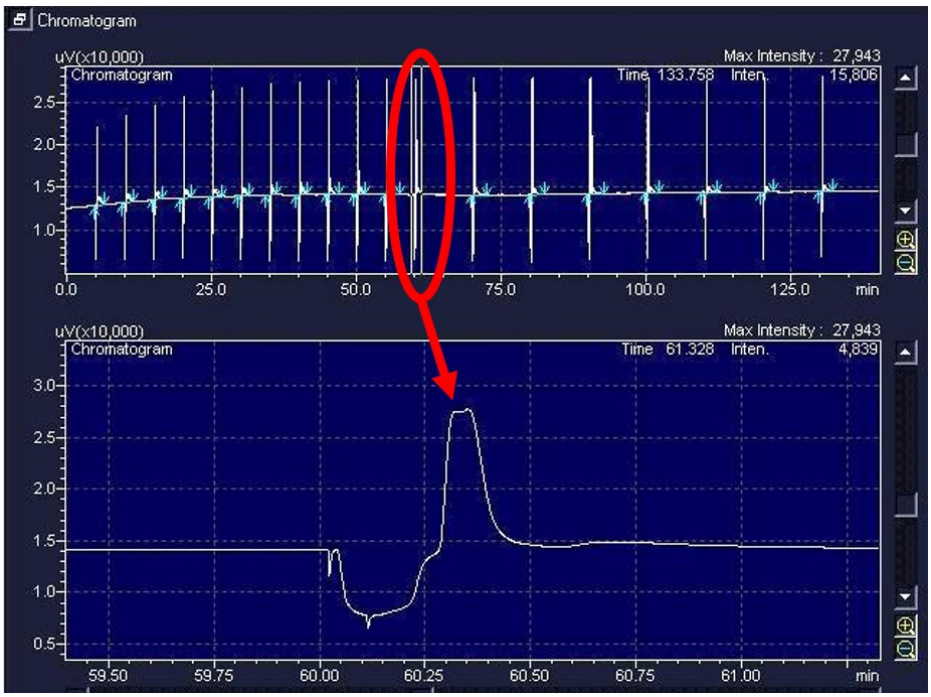



**Figure 2.8:** The real chromatogram obtained from reversal of the carrier gas flow

Previous works (Karaiskakis, 1985; Karaiskakis et al., 1982; Katsanos, 1988; Katsanos and Karaiskakis, 1983; Katsanos et al., 1981) have shown that the relationship between diffusion coefficient and the height, $h$ of the sample peak above the ending baseline was given by the following equation:

$$h = 2\,c_x(l', t_0) = 2Ne^{-\frac{L^2}{4Dt}} \tag{2.3}$$

where $c_x(l', t_0)$ is the concentration of the solute gas at the point $x = l'$, $t_0$ is the total time from the injection of solute to the last backward reversal, $D$ is the diffusion coefficient of the solute into the carrier gas and $N = [mL/\dot{V}(\pi D)]^{1/2}$, where $m$ is the mass injected solute (mol), and $\dot{V}$ is the volume rate flow ($cm^3$/sec). In chromatography, time, $t$ is proportional to the distance travelled by the solute molecules at a given flow rate. Thus, the maximum concentration diminishes with $L$ according to $(1/L)^{1/2}$. The height, $h$, of this

maximum, measured from the ending baseline, gives the sum of $c_2 + c_3$. From Equation 2.3, by replacing $\tau = t'/2$ in these two terms, following equation can be obtained,

$$h = c_2\left(l', t_0 + \frac{t'}{2}\right) + c_3\left(l', t_0 - \frac{t'}{2}\right) \tag{2.4}$$

The two terms of times on the right hand side differ only by *t'*. Since the time interval for such difference is small, both terms can be taken at a mean time, $t_0$. Then the equation (2.4) can be simplified as

$$h \cong 2c(l', t_0) \tag{2.5}$$

### 2.4.2 Quality Assurance/Quality Control of RF-GC Methodology

The uncertainty in the determination of rate coefficients for evaporation mostly depends on the deviation of the temperature control. The uncertainty of the temperature of the chromatograph oven is ± 0.1 K for all experiments. The error in the determination of the diffusion coefficient may come from the measurement of the diffusion column, *L*. Since *D* is proportional to $L^2$ (Gavril et al., 2006; Karaiskakis and Gavril, 2004), small error while measuring the length of the column may contribute to the inaccuracy of the diffusion coefficients determination. The diffusion column, *L*, was measured manually before it was installed in the chromatograph oven and a liquid of accurately known for the diffusion coefficients in the given carrier gas (such as $C_2H_5OH$ in nitrogen gas) was used to calibrate diffusion column. The value of *L,* which was determined at 28.5 cm and was used to estimate unknown diffusion coefficients (Khalid et al., 2012). The determination of the evaporation rate depends also on the accuracy of the length of the diffusion column, *L*.

The nitrogen gas that was used in this experiment was filtered via carrier gas trap and filter (Z-Pure Glass Indicating Moisture Trap, CRS, USA) to remove the moisture in the carrier gas. Furthermore, after running a particular sample, for example, 90% *v*/*v* methanol/water, the experiment was run with an empty bottle by increasing the temperature of the column up to 200 $^{O}$C in order to eliminate any dead volumes at any column junctions of the previous sample. This was to ensure that the columns were empty of any solute remaining from the previous experiment. The chromatogram was ensured to achieve a stable baseline before conducting the reversal process. Also, every rate of coefficients data for this experiment were compared with the FSG theoretical value, and the deviation's value was less than 5%, which is considered as accepted tolerance value.

## 2.5 Surface Tension Measurement

Du Nouy is a method for the determination of liquid's surface tension. Force Tensiometer (Krüss) equipped with Du Nouy platinum iridium ring was used to measure surface tension of the liquid surfactant. This tensiometer employed ring detachment method for the measurement. In this method, a fine torsion head with a gradual dial and a Vernier was used to apply necessary force to pull the platinum-iridium ring from the surface of the solution. The graduated dial and the Vernier permitted reading of the applied force with a precision of ±0.1 mN/m within the range of 0.0 mN/m to 90 mN/m. Platinum-iridium ring of circumference 5.991 cm and ratio of 53.6 between the perimeter and the radius was used for all of the surface tension measurements. The 7 cm diameter, 1.5 cm deep cylindrical dish was used as a container of the selected alcohol and its mixtures. The temperature of the solution was held constant within ± 0.2$^{O}$C by Lauda Ecoline Staredition RE 106 refrigerating bath/circulator (water bath). To minimize the evaporation of the solution inside the sample chamber, the sample chamber was covered by glass panels.

The ring was attached to the clamp located inside the upper part of the sample chamber where there was no obstruction of the ring movements. Then, approximately 60 ml of the sample was placed in the sample vessel which then placed on the adjustable liquid holder inside the sample chamber. The solution was allowed to equilibrate to the experimental temperature. Then, the ring was lifted very slowly (about 0.1 mN/m every 30 seconds) until the ring was lifted and free from the surface of the solution. After the measured surface tension was recorded, the ring was re-immersed into the solution again and prepared for the next reading. All the procedures were done automatically by computer system. The surface tension was measured at least until duplicate values were obtained. The surface tension was measured at least until duplicate values were obtained.

The data acquired from the tensiometer were processed by laboratory desktop software Kruss LabDesk version 3.2-01.

# CHAPTER 3

# RESULTS AND DISCUSSION

## 3.1 Determination of $K_G$ and $D$ by using RFGC

The rate of coefficient for evaporation ($K_G$) of selected alcohols from the pure alcohol liquids and water solutions was calculated based on the sample peaks obtained from the sampling procedures of RF-GC (Figure 2.8). The chromatogram obtained at the end of the sampling procedures was then analyzed. The height ($h$) of the sample peaks from the continuous signal, taken from baseline to the maximum, was plotted as $h$ versus time, giving a diffusion band as shown in Figure 3.1:

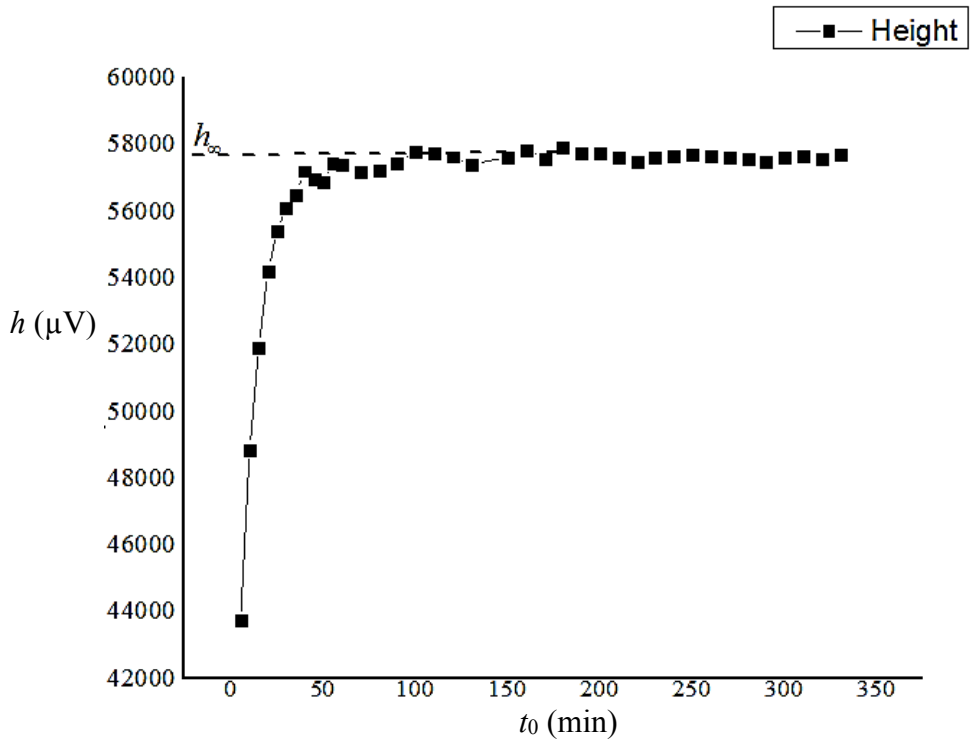



**Figure 3.1:** Plot of sample peaks height, $h$, against time, $t_0$ at 313.15 K and 101325 Pa

Each sample peak was symmetrical and its maximum height $h$ from the baseline is given by equation 3.1:

$$h \cong [2c(l', t_0)]^m \tag{3.1}$$

where m was the response factor for the detector that has been unity for FID. Thus, the concentration of the vapors of an evaporating liquid, c($l'$,$t_0$) at $l'$ and time $t_0$ were proportional to the height ($h$) or the area of the obtained sampling peaks. All these parameters were interrelated to $K_G$, the diffusion coefficient ($D$) and the geometrical details of the diffusion column through the following equation (Karaiskakis and Katsanos, 1984):

$$c(l', t_0) = \frac{K_G D c_0}{V(K_G L + D)}\{1 - exp[-2(K_G L + D)t_0/L^2]\} \tag{3.2}$$

where $L$ is the length of the diffusion column and $v$ the volumetric flow rate of the carrier-gas. From Figure 3.1, the peak reached the steady-state after a period of time. The explanation on the steady-state condition in RF-GC is shown in the Figure 3.2. The steady-state was achieved when there were maximum number of solute molecules (e.g. methanol) been diffused into the stagnant carrier gas inside the diffusion column isothermally. At the beginning of the evaporation process, only a few alcohol molecules available in the diffusion column and the number of molecules will gradually increase until the number of molecules are in "equilibrium" with the carrier gas molecules.

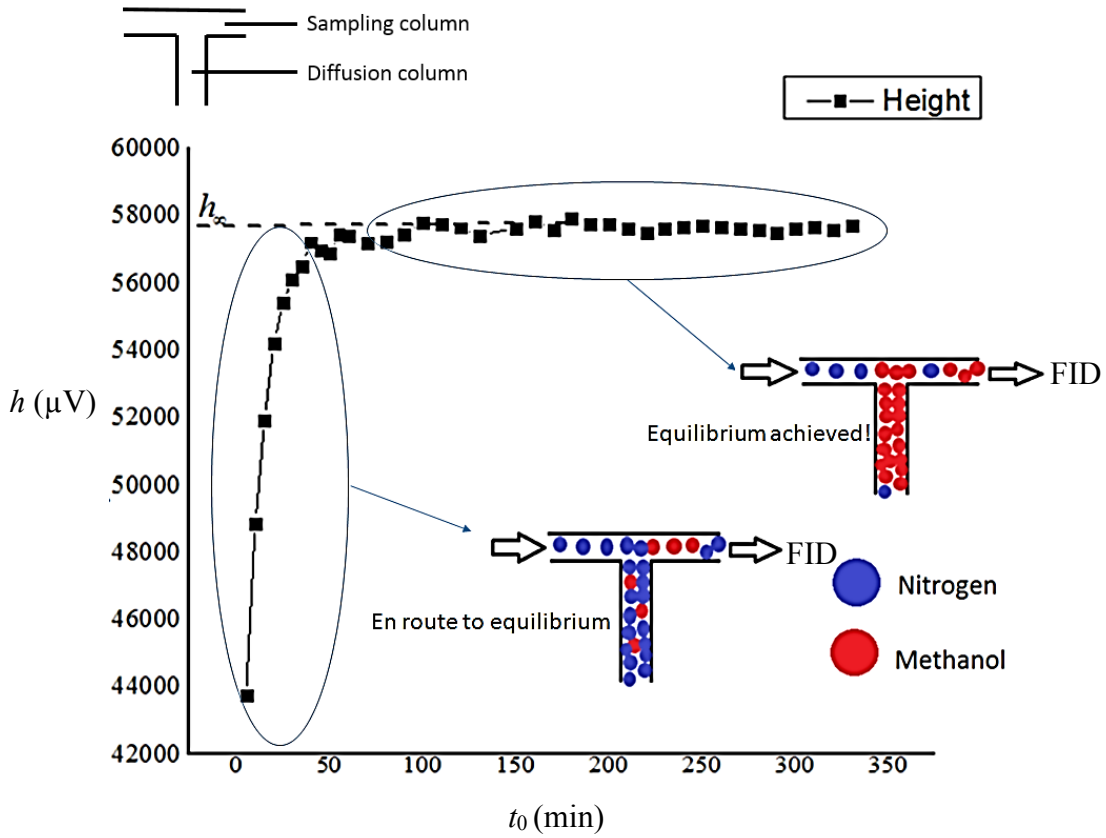



**Figure 3.2:** Evaporation process of selected alcohol in the sampling and diffusion column of RF-GC

From Figure 3.2, at long enough sampling times, an infinite value for the peak height ($h_\infty$) can be obtained. This $h_\infty$ value is used for the linearization by using the following equation (Karaiskakis and Katsanos, 1984):

$$h_\infty = \frac{2K_G D c_0}{[v(K_G L + D)]} \tag{3.3}$$

From the equation 3.3, the following equation can be obtained (Karaiskakis and Katsanos, 1984):

$$\ln(h_\infty - h) = lnh_\infty - \left[\frac{2(K_G L + D)}{L^2}\right] t_0 \tag{3.4}$$

Thus, at long enough sampling times (5 to 350 min), for which Equation (3.4) was derived, a plot of ln ($h_\infty$ - $h$) against $t_0$ will be linear (Figure 3.3), and from its slope the

value of $K_G$ can be calculated from the known value of $L$ (Karaiskakis and Katsanos, 1984).

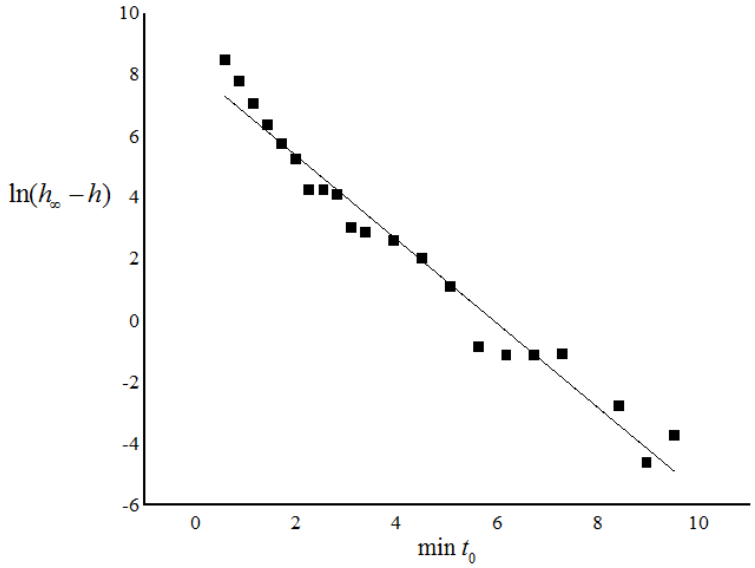



**Figure 3.3:** Example of plot for the diffusion of methanol vapor into carrier gas at 313.15 K and 101325 Pa (v = 1.00 $cm^3$ $s^{-1}$)

Then, the value of $K_G$ can be used to plot a small time period data. For this plot, only the data points from 50 to 80 min from Figure 3.1 which is near to $h_\infty$ were selected. By combining the Equation (3.3) and (3.2), the following equation can be obtained:

$$ln\left[h\left(\frac{L}{2t_0^{\frac{1}{2}}}+K_G t_0^{\frac{1}{2}}\right)\right]=ln\left[\frac{4K_G c_0}{v}\left(\frac{DL}{\pi}\right)^{\frac{1}{2}}\right]-\frac{L^2}{4D}\frac{1}{t_0} \tag{3.5}$$

Now, by using the plot of $ln\left[h\left(\frac{L}{2t_0^{\frac{1}{2}}}+K_G t_0^{\frac{1}{2}}\right)\right]$ versus $\frac{1}{t_0}$, the value for $D$ was calculated from the slope (Figure 3.4).

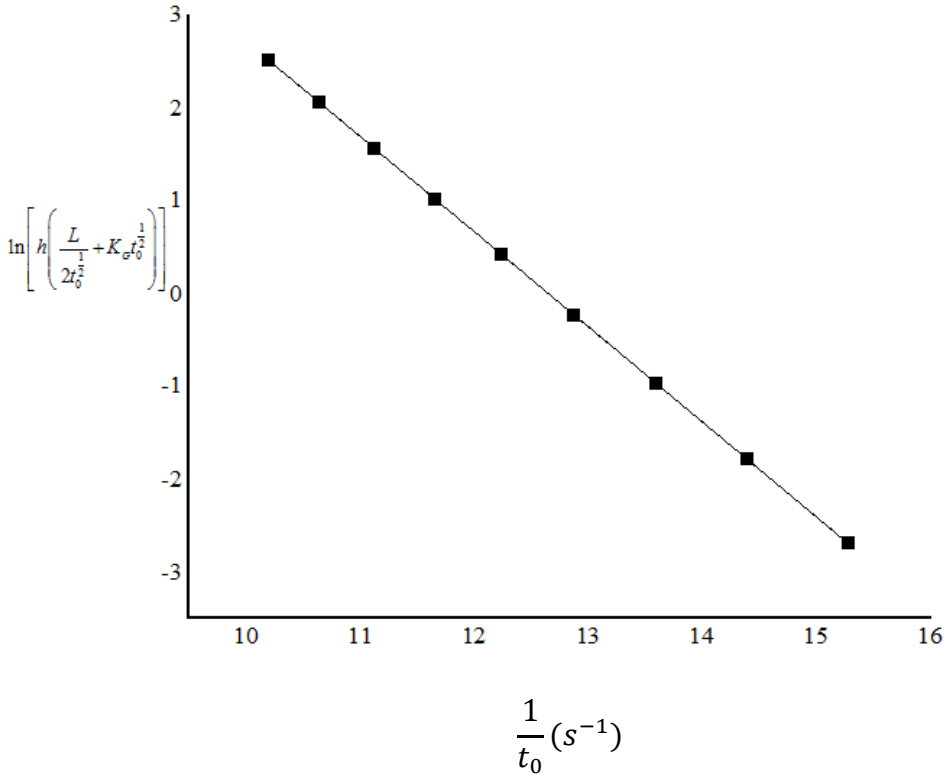



**Figure 3.4:** A plot of $ln\left[h\left(\frac{L}{2t_0^{\frac{1}{2}}}+K_G t_0^{\frac{1}{2}}\right)\right]$ versus $\frac{1}{t_0}$ (determined at 323.15 K and 101325 Pa).

## 3.2 Method Validation

The diffusion coefficient of pure methanol into carrier gas at different temperatures for current work, the data produced by Khalid et al. (2012), and theoretical value were shown in the Figure 3.5. Khalid et al. (2012) used the similar method for the determination of diffusion coefficient (*D*) of pure methanol into nitrogen gas.

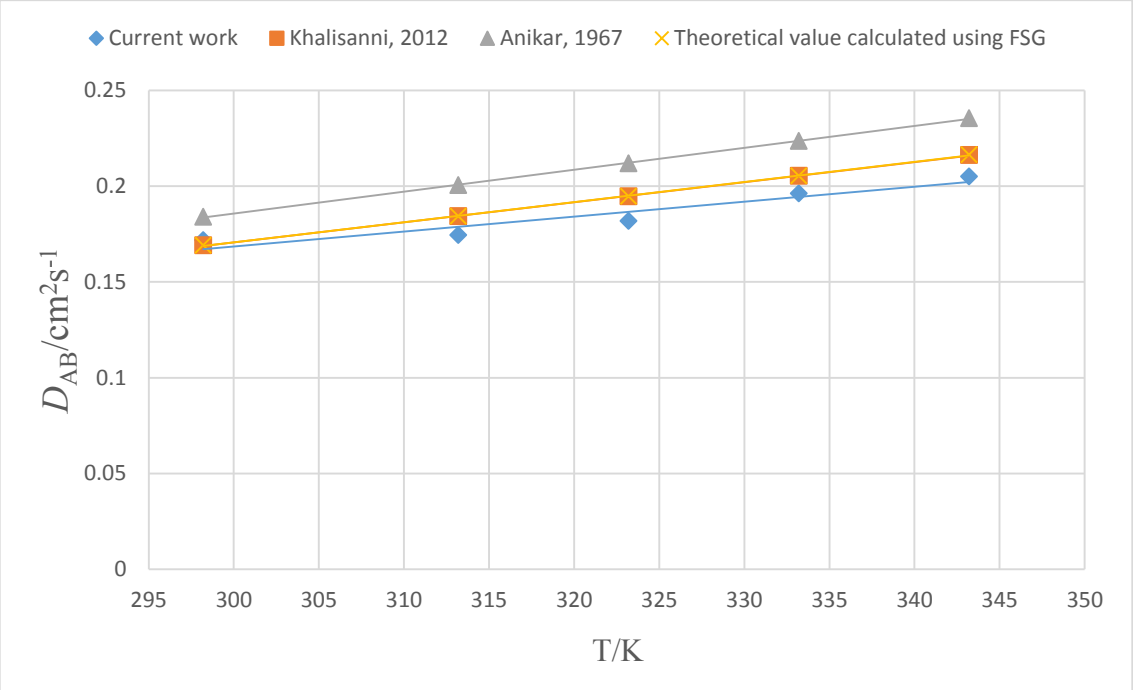



**Figure 3.5:** Comparison of the diffusion coefficient, *D* of pure methanol into nitrogen at different temperatures and at 101325 Pa

Based on Figure 3.5, the variation of *D* with temperature were in agreement with previous work (Khalid et al., 2012) and theoretical values calculated using FSG model. Figure 3.5 shows the diffusion coefficients (*D*) of pure alcohols (methanol, ethanol, 1-propanol and 1-butanol). The diffusion coefficients of pure alcohol were compared with those calculated values using Fuller-Schettler-Giddings (FSG) equation (Fuller et al., 1966). The deviation of the obtained diffusion coefficients from calculated values were calculated using the following equation:

$$Deviation\ (\%) = \left[\frac{\left|D_{present\ work} - D_{theoretical}\right|}{D_{present\ work}}\right] x\ 100 \tag{3.6}$$

The diffusion coefficient values for all selected pure alcohols obtained from this work were in agreements with the values reported by Khalid et al. (2012) and theoretical values. The obtained diffusion coefficients were deviated by 0 – 1.34% from the theoretical values.

**Table 3.1:** The rate coefficients for the evaporation of the alcohol component at various volume percent (% v/v) from alcohol-water mixtures, and diffusion coefficients of the alcohols

| **Alcohol** | **$10^3$ D ($cm^2s^{-1}$)** | | | **Deviation (%)** |
|---|---|---|---|---|
| | **Present work** | **Khalid, 2012** | **Theoretical value** | |
| Methanol | 181.86 ± 0.04 | 184.30 ± 0.70 | 184.31 | 1.34 |
| Ethanol | 140.40 ± 0.09 | 140.04 ± 0.90 | 140.30 | 0.07 |
| 1-propanol | 116.90 ± 0.02 | 119.90 ± 0.20 | 116.90 | 0.00 |
| 1-butanol | 101.00 ± 0.03 | 102.00 ± 0.50 | 102.03 | 1.02 |

The result from this study also indicated that the *D* values were temperature dependence as suggested by Fuller et al. (1966) using the following equation:

$$D_{AB} = \frac{10^{-3}T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{p(V_A^{\frac{1}{3}}+V_B^{\frac{1}{3}})^2} \quad (3.6)$$

where $T$ is temperature in Kelvin, $M_A$ and $M_B$ are molecular weight in g $mol^{-1}$ and $V_A$ and $V_B$ are special diffusion parameter (also known as diffusion volume). Equation 3.6 shows that the diffusion of species A (i.e. methanol) into species B (i.e. nitrogen gas), $D_{AB}$ is directly proportional to temperature, $T$. As the temperature increases, the probability of methanol molecules to collide with the nitrogen molecules in diffusion column of RF-GC is higher, and thus lesser time will be needed for the two molecules to achieve equilibrium (Figure 3.2). In order to understand the types of molecular collision experienced by the molecules in the diffusion column of RF-GC, Karaiskakis (1985) and Gavril et al. (2004) measured the Lennard-Jones parameters by using RF-GC. Based on the result, the

following types of molecular collision in the diffusion columns (cf. Figure 3.2) were suggested.

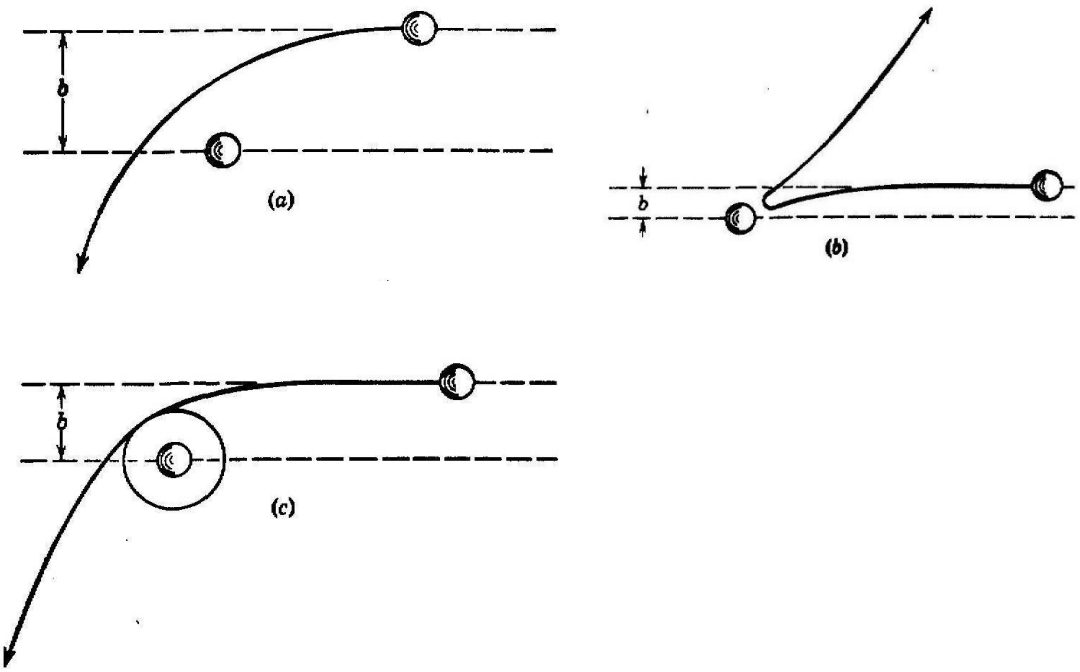



**Figure 3.6:** Types of collision which occur for Lennard-Jones molecules; (a) Grazing collisions in which attractive forces are most important. (b) Almost head-on collision in which the strong repulsive forces come into play. (c) Types of collision in which "orbiting" takes place

## 3.3 Effect of water on the rate of evaporation of alcohol from alcohol/water mixture

### 3.3.1 Effect of alcohol concentration on the rate of evaporation

Volumetric properties of alcohol in water mixtures are different from the pure alcohols (Chodzin´ska et al., 2012; Franks and Ives, 1966). The interaction between the water and alcohol molecules via hydrogen bonding will influence the adsorption of alcohol molecules at the surface of the aqueous solution (Chodzin´ska et al., 2012; Yano, 2005; Zana, 1995). On the other hand, the strength of the hydrogen bonding between the alcohol and the water molecules is highly depending on the type of alcohol in the aqueous solution (Bowron and Moreno, 2003; Dolenko et al., 2010; Pártay et al., 2007). In this study, the effect of methanol and ethanol concentration on the rate of evaporation were evaluated.

Table 3.2 and 3.3 show the effect of water fraction on $K_G$ of methanol and ethanol at 313.15 K. Based on the results, the variation of $K_G$ values of methanol and ethanol at different concentration (% v/v) are shown in Figure 3.7 and Figure 3.8 respectively. The $K_G$ of methanol was found to increase with increasing methanol concentration from 80 to 90% (v/v) (Figure 3.7 and Table 3.2) due to the increasing available methanol for evaporation. However, at 95% (v/v), $K_G$ of methanol was found to decrease and it was proposed that at this concentration, methanol molecules tend to form dimers and trimmers in bulk aqueous solution (Dixit et al., 2000). As a result, the stronger hydrogen bond between methanol molecules was formed favorably as compared to the methanol and water. Isothermally, when enough energy was supplied to this aqueous solution, only small amounts of methanol molecules that bonded to water molecules via weaker hydrogen bonding will be broken, resulting in lesser methanol molecules to escape from the liquid's surface and therefore reduced the $K_G$ of methanol.

At 95% v/v concentration, the formation of hydrogen bond between ethanol and water molecules was less favorable as compared to methanol molecule. The weaker interaction between water and ethanol molecules resulting more ethanol molecules moves toward the surface of the mixture. As a result, more ethanol molecules will be able to populate at the liquid surface (Yano, 2005). When the concentration of ethanol in aqueous solution increased, the $K_G$ of ethanol was also increased since more ethanol molecules were available at the liquid's surface. High populations of ethanol molecules at the liquid's surface will increase the chance for the ethanol molecules to escape from the liquid's surface. According to Vaquez et al. (1995), the surface tension of ethanol-water mixture decreased as the concentration of ethanol increased as indicated in Figure 3.8 and Table 3.3. This result suggested that more ethanol molecules will be populated at the liquid's surface as the concentration of ethanol increases (Wakisaka and Iwakami, 2014) and consequently enhanced the ethanol evaporation.

**Table 3.2:** $K_G$ for methanol that containing in water

| **Alcohol** | **T (K)** | **Concentration (% v/v)** | **$10^2 K_G$ (cm $s^{-1}$)** |
|---|---|---|---|
| Methanol | 313.15 | 95 | 47.10 ± 0.13 |
| | | 90 | 61.91 ± 0.15 |
| | | 85 | 55.20 ± 0.16 |
| | | 80 | 44.53 ± 0.02 |

**Table 3.3:** $K_G$ for ethanol that containing in water.

| **Alcohol** | ***T* (K)** | **Concentration (% v/v)** | **$10^2 K_G$ (cm $s^{-1}$)** |
|---|---|---|---|
| Ethanol | 313.15 | 95 | 70.92 ± 0.15 |
| | | 90 | 47.51 ± 0.89 |
| | | 80 | 45.11 ± 0.08 |

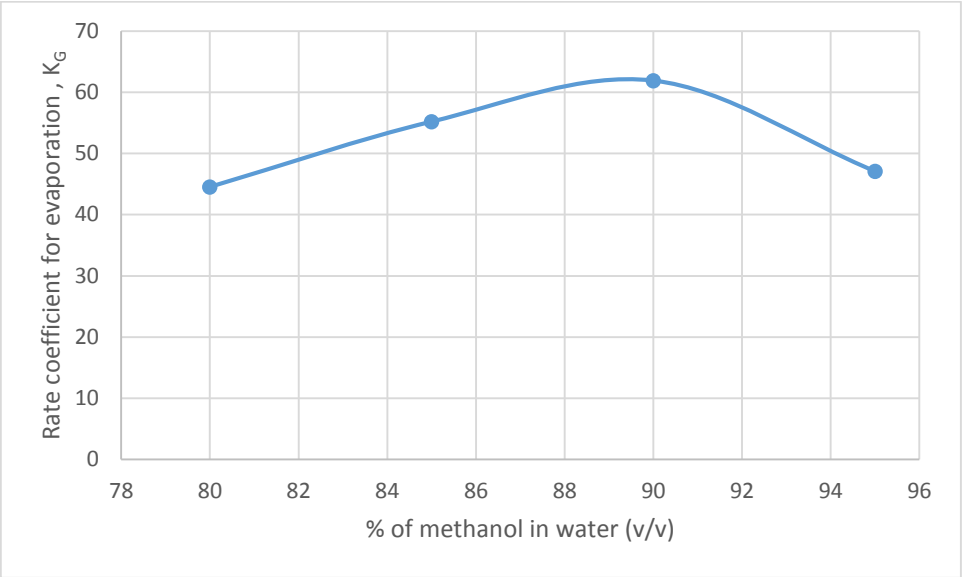



**Figure 3.7:** The effect of the concentration of methanol in water (v/v) on $K_G$ at 313.15 K.

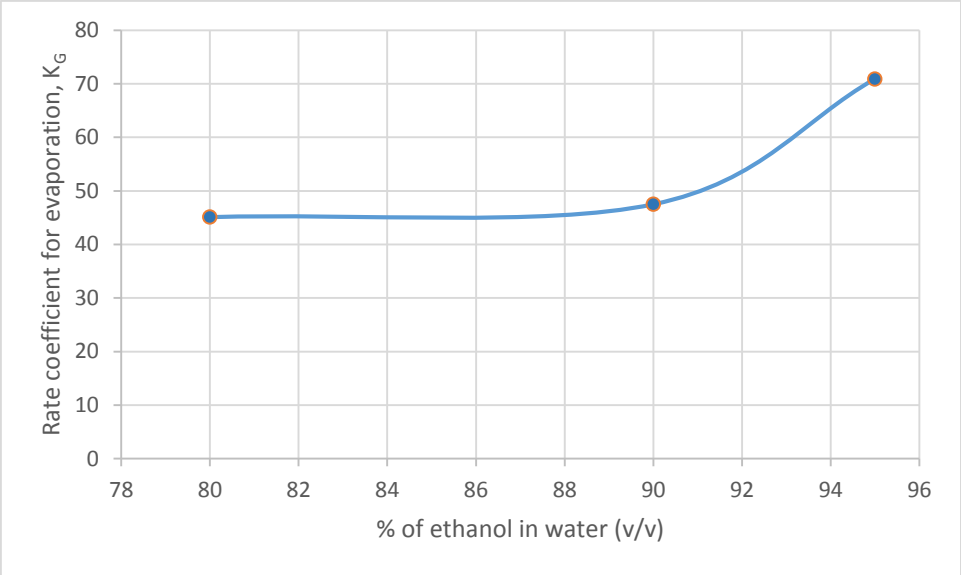



**Figure 3.8:** The effect of the concentration of ethanol in water (v/v) on $K_G$ at 313.15 K.

### 3.3.2 Effect of temperature on the rate of evaporation

For evaporation, certain fraction of the molecules that possess enough kinetic energy to overcome the forces of attraction by the surrounding molecules will escape from the surface of the liquid. Therefore, temperature which is the main source of energy is an important parameter that influence the evaporation (Jozsef, 2009). At higher temperature, the alcohol molecules with higher average kinetic energy will populate at the surface of the liquid. More molecules will have higher kinetic energy than the average kinetic energy and these molecules tend to escape from the liquid surface, while some others possess lower kinetic energy than the average and remained in the solution.

Table 3.4 shows the $K_G$ of methanol and ethanol at temperature ranging from 313.15 to 333.15 K. Even with the present of water, $K_G$ of methanol and ethanol were found to increase with temperature. In this case, when the temperature increased, more alcohol molecules at the liquid's surface obtained enough kinetic energy to overcome the attraction force between surrounding molecules and more alcohol molecules were escaped from the liquid's surface.

**Table 3.4:** Effect of temperature on $K_G$ for methanol and ethanol in water

| Alcohol | Concentration (% *v*/*v*) | $K_G$ at different temperature | | |
|---|---|---|---|---|
| | | 313.15 K | 323.15 K | 333.15 K |
| Methanol | 95 | 47.10 ± 0.13 | 58.04 ± 0.31 | 68.97 ± 0.24 |
| | 90 | 61.91 ± 0.15 | 138.81 ± 0.46 | 142.34 ± 0.88 |
| | 85 | 55.20 ± 0.16 | 135.70 ± 0.07 | 139.93 ± 0.36 |
| | 80 | 44.53 ± 0.02 | 123.83 ± 0.11 | 133.66 ± 0.29 |
| Ethanol | 95 | 70.92 ± 0.15 | 84.83 ± 0.09 | 123.42 ± 0.06 |
| | 90 | 47.51 ± 0.89 | 71.01 ± 0.12 | 94.49 ± 0.07 |
| | 80 | 39.86 ± 0.04 | 40.51 ± 0.03 | 45.11 ± 0.08 |

Table 3.5 shows the diffusion coefficients ($D$) of methanol and ethanol determined from various alcohol-water mixtures at different temperatures. $D$ for methanol and ethanol were found to increase with increasing temperature as predicted by

Equation 3.6. Equation 3.6 showed that the diffusion coefficient is directly proportional to the temperature. When the temperature increases, the frequency for each alcohol molecules that escaped from the liquid's surface to collide with stagnant carrier gas in the diffusion column will also increase. Thus, the time taken for each alcohol molecule to travel along the diffusion column will be shortened. At higher temperature, more alcohol molecules will gain enough kinetic energy to travel along the diffusion column. As a result, the diffusion rate for alcohol into the carrier gas will be increased with increasing temperature.

**Table 3.5:** Diffusion coefficient for methanol and ethanol at various volume percent (% *v*/*v*) from alcohol-water mixtures at different temperatures

| **Alcohol** | **Concentration (% *v*/*v*)** | ***D* at different temperature** | | |
|---|---|---|---|---|
| | | **313.15 K** | **323.15 K** | **333.15 K** |
| Methanol | 95 | 182.86 ± 0.04 | 191.77 ± 0.08 | 202.32 ± 0.09 |
| | 90 | 181.86 ± 0.03 | 198.13 ± 0.44 | 208.79 ± 0.18 |
| | 85 | 187.60 ± 0.02 | 192.31 ± 0.01 | 203.31 ± 0.03 |
| | 80 | 184.12 ± 0.02 | 203.64 ± 0.02 | 204.17 ± 0.02 |
| Ethanol | 95 | 113.28 ± 0.07 | 149.74 ± 0.02 | 157.34 ± 0.02 |
| | 90 | 146.88 ± 0.09 | 149.17 ± 0.01 | 159.87 ± 0.02 |
| | 80 | 139.65 ± 0.01 | 147.99 ± 0.01 | 156.06 ± 0.01 |

### 3.3.3 Effect of carbon number of alcohol on $K_G$

Table 3.6 shows the $K_G$ values obtained with the pure alcohols (methanol, ethanol, 1-propanol and 1-butanol), as well as their water mixtures at 313.15 K. The current study only focused on the straight chain alcohols, since it has been widely used in various applications (Cheng and Timilsina, 2011). The results showed that the $K_G$ values of selected alcohol were the highest for pure alcohols. The presence of water largely reduced the $K_G$ of methanol, ethanol and 1-propanol (Figure 3.9). O'Hare and Spedding (1992) suggested that the evaporation of the alcohol components, comprising a binary mixture where the water was presence, could be predicted in terms of vapour pressure. They suggested that the vapour pressure of alcohol mixture acted as a driving force in a similar way as pure alcohol evaporation. According to O'Hare and Spedding (1992), the vapour pressure contributed by the alcohol's molecules became more significant as compared to the water molecules in the alcohol mixture when the alcohol components are in the range of 30-100% *w*/*w* in the mixture. The fact that the $K_G$ values for 1-butanol were the lowest since 1-butanol possessed the lowest vapour pressure as compared to other alcohols (Table 3.6). Since 1-butanol possesses the lowest vapour pressure, thus, 1-butanol is less volatile alcohol as compared to the other selected alcohols. The presence of water also does not significantly influence the $K_G$ of 1-butanol and this result further indicated that the evaporation of 1-butanol is determined by its vapour pressure.

**Table 3.6:** $K_G$ values for methanol, ethanol, 1-propanol and 1-butanol at various concentrations (% *v*/*v*) determined at 313.15 K

| **Alcohol** | **Volume percent (% *v*/*v*)** | **$10^2 K_G$ (cm $s^{-1}$)** |
|---|---|---|
| Methanol | 100 | 96.69 ± 0.20 |
| | 95 | 47.10 ± 0.13 |
| | 90 | 61.91 ± 0.15 |
| Ethanol | 100 | 175.58 ± 0.07 |
| | 95 | 70.92 ± 0.15 |
| | 90 | 47.51 ± 0.89 |
| 1-propanol | 100 | 190.94 ± 0.15 |
| | 95 | 70.79 ± 0.16 |
| | 90 | 74.12 ± 0.04 |
| 1-butanol | 100 | 54.51 ± 0.19 |
| | 95 | 50.23 ± 0.09 |
| | 90 | 61.77 ± 0.15 |

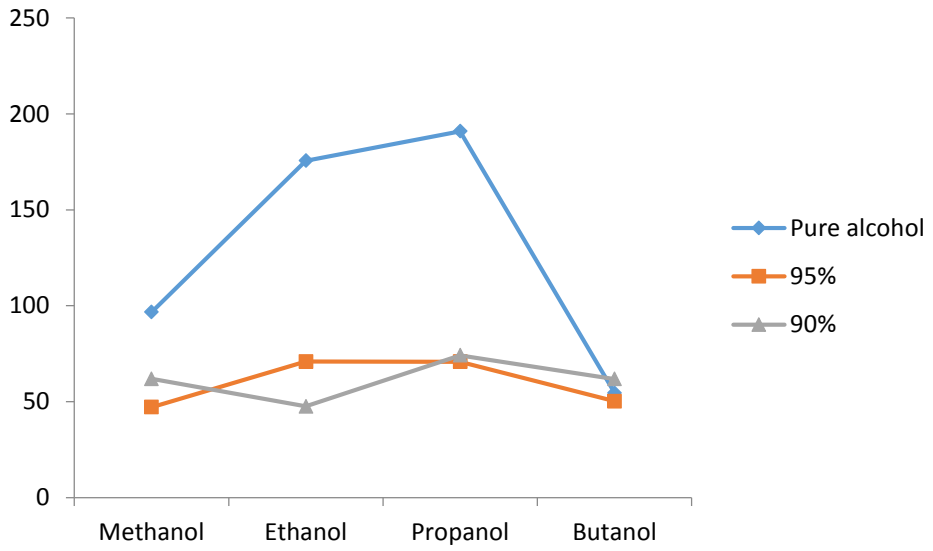



**Figure 3.9:** Variation of $K_G$ at 313.15 K for selected alcohol determined using pure alcohols, 95% alcohol in water and 90% alcohol in water.

As shown by Figure 3.9 and Table 3.6, this result showed that the evaporation process was highly dependent on the number of carbon or the molecular weight of the selected alcohols. In general, ethanol and 1-propanol are the most volatile alcohol when it appeared as pure liquid and with the presence of 5% water. For 90% of alcohols in water different trend of $K_G$ variation was observed (Figure 3.9) and ethanol was found to

possess the lowest $K_G$. Previous studies (Brown et al., 1969; Hu et al., 2010; O'Hare et al., 1993) have reported that ethanol possessed the lower evaporation rates as compared to 1-propanol was mainly due to the hydrogen bonding that makes the hydroxyl group of ethanol being “trapped” in a fluctuation clathrate structure.

In conclusion, ethanol and 1-propanol were the most volatile selected alcohols when these alcohol present as pure liquid and alcohol-water mixture with the concentration of 95% selected alcohols. With the presence of 10% water, different trend of $K_G$ variation was observed. The $K_G$ of selected alcohols determined from 90% of alcohol in water mixtures increased based on the following trends:

Ethanol < 1-butanol < methanol < 1-propanol



Rate coefficient for evaporation increases

### 3.3.4 Activation energy for evaporation

Arrhenius equation has been used to investigate the effect of absolute temperature on the rate constant of chemical reactions (Atkins and Paula, 2006). In this study, the Arrhenius equation was used to calculate the activation energy that required for the selected alcohols to evaporate. In Arrhenius equation (Equation 3.7), $k$ which is the reaction rate constant can be used to represent $K_G$ (cm $s^{-1}$), $E_a$ which is the activation energy can be used to represent the minimum energy that required by alcohol to evaporate from the liquid surface (J $mol^{-1}$), $T$ is temperature of the liquid (Kelvin), $R$ is the constant (8.3145 J $mol^{-1}$ $K^{-1}$) and $A$ is an arbitrary constant,

$$\ln k = \ln A - \frac{E_a}{RT} \tag{3.7}$$

When the rate constant of a reaction obeyed Arrhenius equation, a plot of ln $k$ versus $T^{-1}$ will give a straight line. The slope that represents $-E_a/R$ can be used to determine the activation energy, $E_a$. Figure 3.10 shows the plot of ln ($K_G$) versus temperature of selected alcohols in water with the concentration of 90% (v/v) and straight line was obtained for all selected alcohol and this result further indicated that evaporation of alcohol from water was in agreement with Arrhenius equation. The activation energy was calculated from the slope in the given temperature range. The values $E_a$ for the selected alcohols are summarized in fourth column of Table 3.7.

**Table 3.7:** $E_a$ and $K_G$ at various temperatures for 90% of selected alcohol in water

| **Alcohol** | ***T*** **(K)** | $\mathbf{10^2}$ $\boldsymbol{K}_{\mathbf{G}}$ **(cm** $\mathbf{s^{-1}}$**)** | $\boldsymbol{E}_{\mathbf{a}}$ **(kJ** $\mathbf{mol^{-1}}$**)** |
|---|---|---|---|
| Methanol | 308.15 | 26.45 ± 0.01 | 84.2 |
| | 313.15 | 61.91 ± 0.15 | |
| | 318.15 | 84.53 ± 0.01 | |
| | 321.15 | 125.86 ± 0.01 | |
| | 323.15 | 138.81 ± 0.46 | |
| Ethanol | 313.15 | 47.51 ± 0.89 | 27.7 |
| | 323.15 | 71.01 ± 0.12 | |
| | 333.15 | 94.49 ± 0.07 | |
| | 343.15 | 141.77 ± 0.44 | |
| | 353.15 | 170.68 ± 0.07 | |
| | 363.15 | 199.44 ± 0.12 | |
| 1-propanol | 313.15 | 74.12 ± 0.04 | 10.9 |
| | 323.15 | 83.36 ± 0.02 | |
| | 333.15 | 92.17 ± 0.68 | |
| | 343.15 | 104.40 ± 0.02 | |
| | 353.15 | 125.61 ± 0.04 | |
| | 363.15 | 126.58 ± 0.27 | |
| 1-butanol | 313.15 | 61.77 ± 0.15 | 8.4 |
| | 323.15 | 71.44 ± 0.19 | |
| | 333.15 | 72.56 ± 0.04 | |
| | 343.15 | 82.52 ± 0.03 | |
| | 353.15 | 91.33 ± 0.02 | |
| | 363.15 | 97.14 ± 0.09 | |
| | 373.15 | 104.54 ± 0.12 | |

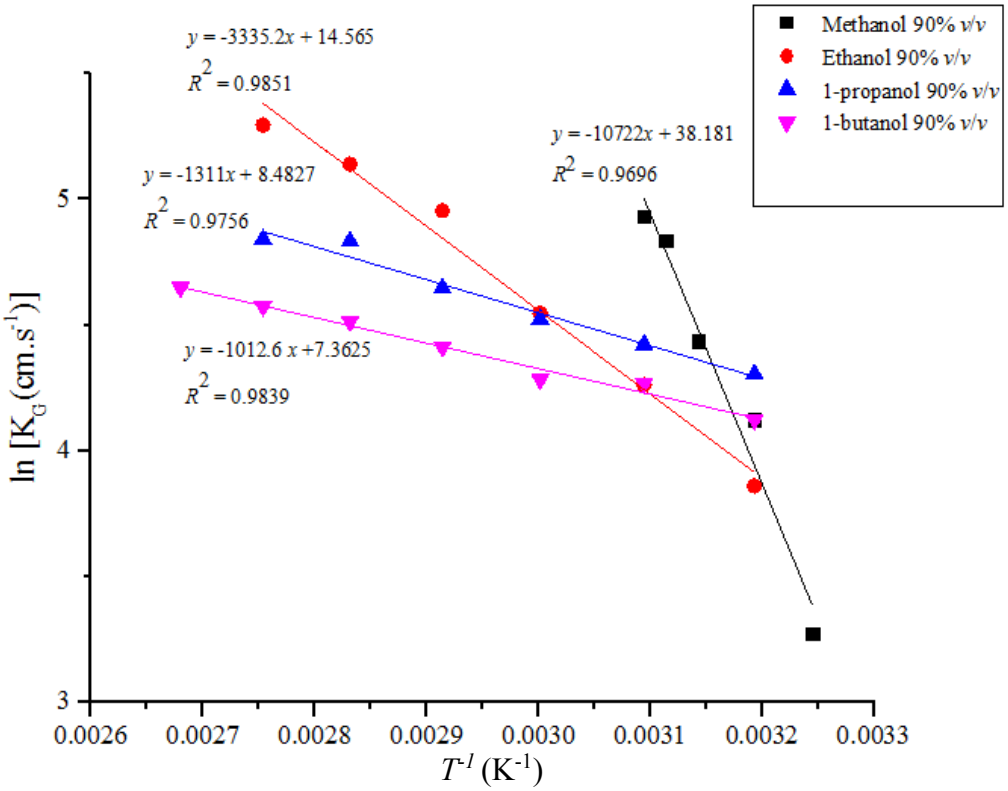



**Figure 3.10:** Temperature dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures.

According to Figure 3.10, the slope of the plot decreases with increasing number of carbon of alcohol from methanol to 1-butanol. This result indicated that the energy that required for the alcohol to evaporate was decreased with increasing carbon number of selected alcohols as shown in Table 3.7. Short chain alcohols such as methanol and ethanol are very soluble in water. This is due to the hydroxyl group in the alcohol which is able to form hydrogen bond with water molecules. With increasing carbon chain length, 1-propanol and 1-butanol decrease in solubility due to the formation of hydrogen bonds between alcohol molecules as these molecules are more tightly packed together as the size and mass of alcohol increase (Hill and Holman, 2000). Therefore, methanol and ethanol required higher energy (or higher $E_a$) to break the hydrogen bond between alcohol-water which is stronger than the hydrogen bond between alcohol molecules for 1-propanol and 1-butanol. Previous studies (Karaiskakis et al., 1986) reported the $E_a$ value for pure methanol and 1-butanol as 31.0 and 5.0 kJ $mol^{-1}$, respectively. The $E_a$ for the

methanol and 1-butanol in water mixture (90% *v*/*v*) was found to be higher than the pure methanol and 1-butanol. This result further proved that the formation of hydrogen bond between water and alcohol molecules is stronger than the hydrogen bond between the alcohol molecules.

## 3.4 Evaporation of alcohol with the presence of surfactant

This study focused on the effect of surfactants on $K_G$ of selected alcohol. The first part of this study was focused on the effect of Triton X-100 on the $K_G$ of pure alcohols. For this study, Triton X-100 at different concentrations were mixed into methanol and ethanol. Triton X-100 was selected for this study because it is a commonly used surfactant in cleaning process that ranging from industrial and agrochemical products (Rosen, 1989). This surfactant belongs to the alkyl polyethylene oxide group (Zdziennicka, 2009). Besides that, Triton X-100 is able to form an insoluble surfactant layer when mixed with alcohol (Gavril et al., 2006) and thus, Triton X-100 is expected to suppress $K_G$ of the alcohols.

The second part of this study was focused on the effect of non-ionic, anionic and cationic surfactants on the $K_G$ of methanol containing in methanol-water mixtures. This study can provide the suitable surfactants that can be used to suppress methanol from been evaporated from 24% methanol in water. US Environmental Protection Agency's defined the waste methanol in concentration equal or greater than 24% by weight is considered as an ignitable hazardous waste (USEPA, 1994; MI, 2014).

### 3.4.1 Effect of Triton X-100 on the evaporation of methanol and ethanol

The results for $K_G$ and $D$ measurement of the pure methanol and pure ethanol with the presence of Triton X-100 at different temperatures are shown in Table 3.8 to Table 3.11.

**Table 3.8:** $D$ values of pure methanol at different temperature ranging from 313.15 K to 333.15 K

| Triton X concentration (g/ml) | $D$ at different temperature ($cm^2s^{-1}$) | | |
|---|---|---|---|
| | 313.15 K | 323.15 K | 333.15 K |
| 0 | 181.86 ± 0.04 | 196.18 ± 0.04 | 205.05 ± 0.03 |
| 6.36 | 189.23 ± 0.02 | 198.81 ± 0.02 | 208.98 ± 0.02 |
| 12.72 | 188.07 ± 0.02 | 193.61 ± 0.02 | 204.68 ± 0.03 |
| 19.08 | 183.14 ± 0.02 | 185.80 ± 0.01 | 212.57 ± 0.02 |
| 25.44 | 189.46 ± 0.02 | 188.61 ± 0.03 | 209.75 ± 0.02 |

**Table 3.9:** $D$ values for pure ethanol at different temperature ranging from 313.15 K to 343.15 K

| Triton X concentration (g/ml) | $D$ at different temperature ($cm^2s^{-1}$) | | | |
|---|---|---|---|---|
| | 313.15 K | 323.15 K | 333.15 K | 343.15 K |
| 0 | 140.40 ± 0.09 | 148.30 ± 0.06 | 156.30 ± 0.03 | 164.80 ± 0.09 |
| 6.36 | 141.36 ± 0.02 | 147.16 ± 0.00 | 153.79 ± 0.03 | 166.98 ± 0.03 |
| 12.72 | 141.59 ± 0.03 | 147.94 ± 0.02 | 155.22 ± 0.03 | 162.07 ± 0.03 |
| 19.08 | 141.02 ± 0.02 | 146.24 ± 0.02 | 156.76 ± 0.03 | 162.66 ± 0.03 |
| 25.44 | 140.90 ± 0.02 | 146.70 ± 0.02 | 154.20 ± 0.02 | 161.55 ± 0.03 |

**Table 3.10:** $K_G$ values for pure methanol at different temperature ranging from 313.15 K to 343.15 K

| Triton X concentration (g/ml) | $K_G$ at different temperature (cm $s^{-1}$) | | |
|---|---|---|---|
| | 313.15 K | 323.15 K | 333.15 K |
| 0 | 96.69 ± 0.20 | 106.76 ± 0.29 | 107.15 ± 0.44 |
| 6.36 | 31.75 ± 0.05 | 48.04 ± 0.18 | 59.69 ± 0.39 |
| 12.72 | 20.72 ± 0.14 | 42.50 ± 0.23 | 51.15 ± 0.29 |
| 19.08 | 17.31 ± 0.07 | 6.19 ± 0.04 | 7.38 ± 0.25 |
| 25.44 | 12.30 ± 0.31 | 5.47 ± 0.14 | 7.10 ± 0.07 |

**Table 3.11:** $K_G$ values for pure ethanol at different temperature ranging from 313.15 K to 343.15 K

| Triton X concentration (g/ml) | $K_G$ at different temperature (cm $s^{-1}$) | | | |
|---|---|---|---|---|
| | **313.15 K** | **323.15 K** | **333.15 K** | **343.15 K** |
| 0 | 175.58 ± 0.07 | 185.02 ± 0.09 | 195.11 ± 0.05 | 206.08 ± 0.04 |
| 6.36 | 136.30 ± 0.10 | 145.26 ± 0.21 | 171.32 ± 0.22 | 189.22 ± 0.22 |
| 12.72 | 90.42 ± 0.25 | 113.77 ± 0.07 | 106.33 ± 0.25 | 167.58 ± 0.26 |
| 19.08 | 85.01 ± 0.19 | 107.22 ± 0.16 | 101.76 ± 0.30 | 159.88 ± 0.47 |
| 25.44 | 80.59 ± 0.64 | 99.09 ± 0.37 | 85.96 ± 0.29 | 143.79 ± 0.33 |

The results showed that the addition of triton X-100 gives no effect to the *D* values of the selected alcohols (Gavril et al., 2006). The *D* values by mean of RF-GC were calculated based on the diffusivity of the solute into the carrier gas. Thus, the movement of the molecules across the surfactant was not considered in the *D* calculation. The *D* values in this case were calculated after the molecule leaving the bulk.

With the presence of Triton X-100, there are two possible factors that influence the evaporation rate: (1) the stagnant gaseous in diffusion column and (2) surfactant layers that located at the interphase where the solute diffused (Gavril et al., 2006; Mohammad et al., 2013). Figure 3.11 and Figure 3.12 show the plots of the percent reduction of $K_G$ for methanol and ethanol versus the concentration of Triton X-100. In general, the retardation of $K_G$ for methanol and ethanol were found to increase with increasing Triton-X concentration. This retardation was due to the presence of surfactant layer (Gavril et al., 2006; Mohammad et al., 2013). During the evaporation process, the alcohol molecules have to diffuse through the "*free*" space across the surfactant molecules before evaporation (Figure 3.13). Therefore, by increasing the concentration of the Triton X-100, the thickness of the surfactant layer on the mixture's surface will be increased. Therefore, the distance for the alcohol molecules to travel across the surfactant layer will be increased and consequently reduced the value of $K_G$.

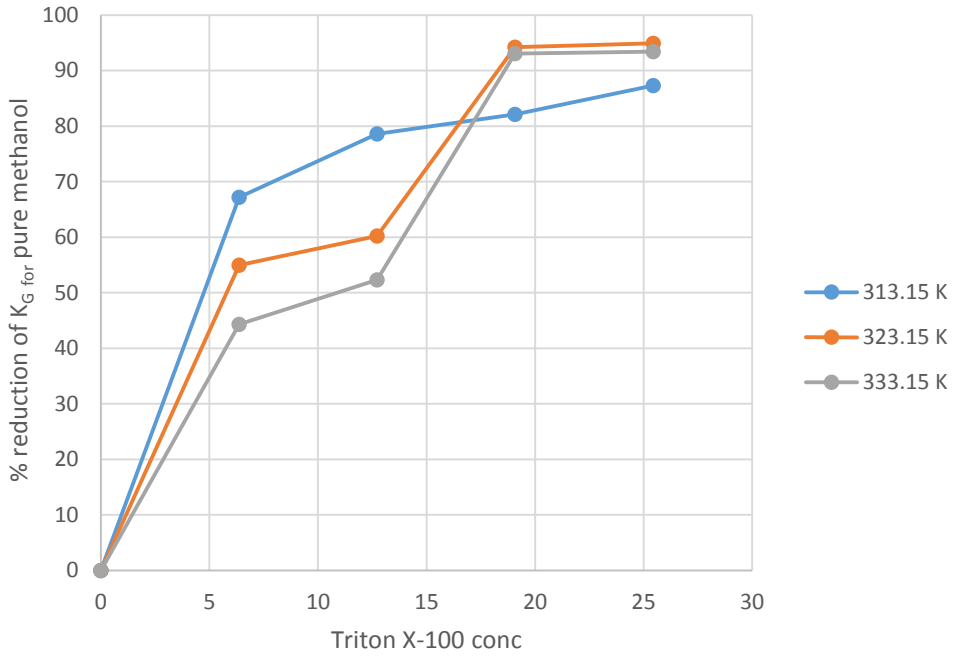



**Figure 3.11:** Percent reduction of $K_G$ for pure methanol with the presence of Triton X-100 at different temperature.

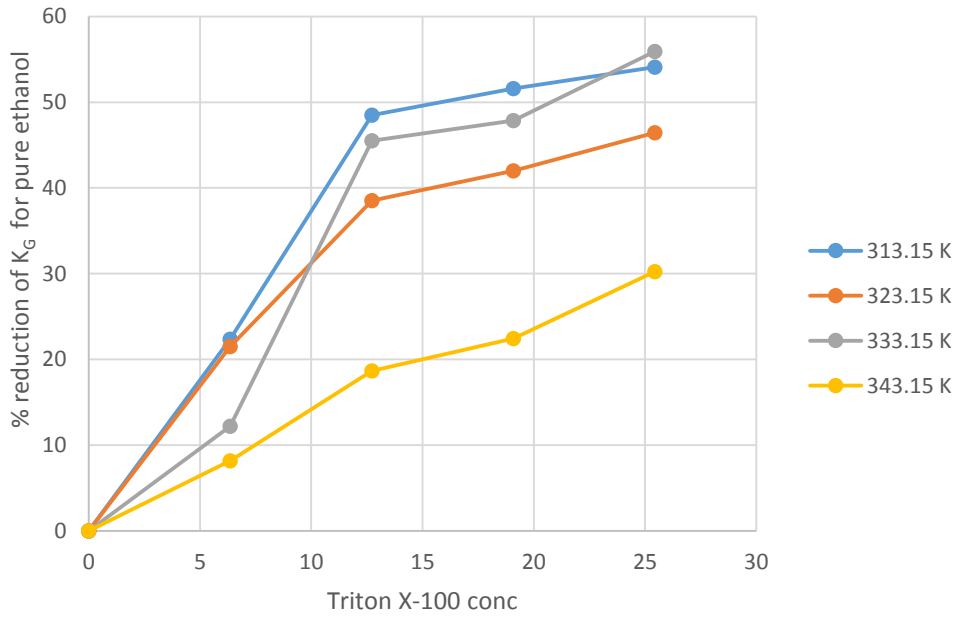



**Figure 3.12:** Percent reduction of $K_G$ for pure ethanol with the presence of Triton X-100 at different temperature.

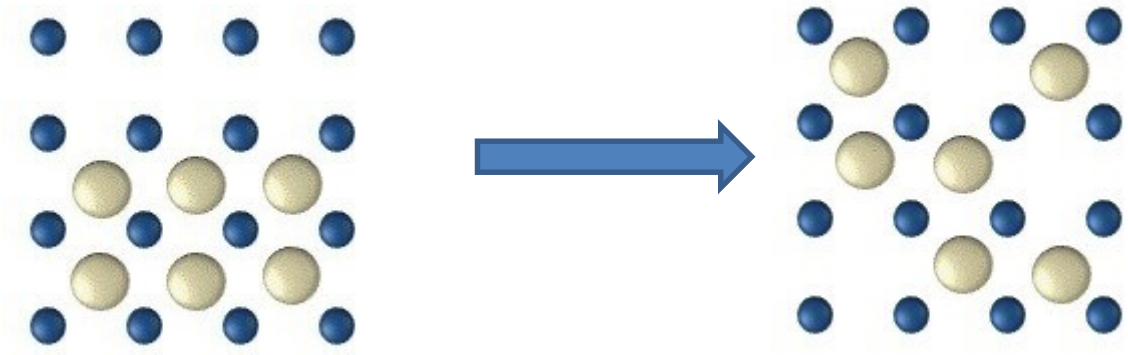


**Figure 3.13:** Movement of alcohol molecules (white circles) across the surfactant layers (blue circles).

The addition of Triton X-100 gives lesser effects on the evaporation of ethanol as compared to methanol. In other words, the rate of methanol evaporation can be reduced more effectively as compared with ethanol. Triton X-100 is a non-ionic surfactant, the surface-active portion bears no apparent ionic charge, and thus it adsorbs onto the surfaces of alcohol with the hydrophobic group oriented toward the surface (Gavril et al., 2006). Since methanol has higher dielectric (Gregory and Clarke, 2005; Mohsen-Nia et al., 2010) and dipole moment (Lide, 2008) as compared to ethanol, methanol has higher ability to donate its uncoupled electron pairs to form hydrogen bond with the hydrophilic group of the Triton X-100. Therefore, as methanol move along the surfactant layer, higher energy was required for it to evaporate from the surfactant layer as compared with ethanol.

### 3.4.2 Effect of non-ionic, anionic and cationic surfactants on the evaporation of methanol from methanol/water mixture

The addition of surfactant to the methanol-water mixture causes the unfavorable orientation of the water and methanol molecules around the hydrophobic chains of surfactant and decreases the solution entropy. As the less structured system is more favorable, surfactant molecules tend to move to the solution–air interface and become oriented in such a way that their hydrophilic heads stay in contact with methanol-water mixture and their hydrophobic chains get in contact with air (Figure 3.14). The adsorption of surfactant at that interface causes the reduction of the surface tension of methanol-water mixture (Bielawska et al., 2015). With the presence of surfactant, the evaporation of methanol from bulk aqueous solution required three steps (Figure 3.15) for the methanol molecules to move from inner bulk liquid phase to the outer gaseous phase (Rusdi and Moroi, 2004): (1) the movement into an area just beneath the liquid surface by self-diffusion through the aqueous phase, (2) the movement acrosses the surfactant layer, and (3) the movement from the surfactant layer into the gaseous phase. Thus, in this case, one additional process (STEP 2) is required for methanol to evaporate into the gaseous phase as compared to the pure alcohols and alcohol-water mixtures.

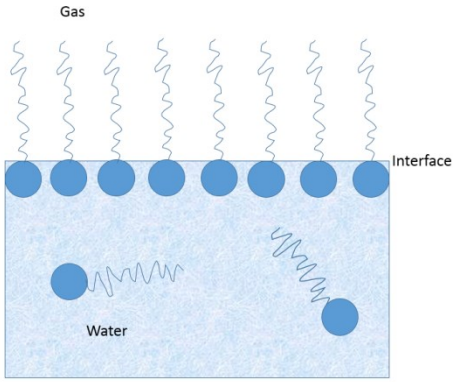



**Figure 3.14:** Conventional model of surfactant solution at the gas-liquid interface

Concentration of methanol molecules is decreasing from the initial concentration value, $C_0$, as the alcohol molecules travel from the bulk aqueous phase to the gaseous phase (indicated by the curve in STEP 1 in the Figure 3.15). The red curve represents the concentration of alcohol molecules is also discontinued when the alcohol molecules move into the surfactant's layer. This is because the alcohol molecules required additional energy in order to cross a liquid/gas interphase that covered by a surfactant layer (STEP 2 in Figure 3.15). Majority of the methanol molecules in the surfactant layer will spend their time in this region. Only the methanol molecules that possess enough energy are able to escape from the interphase and directly go to the gaseous phase as indicated by STEP 3.

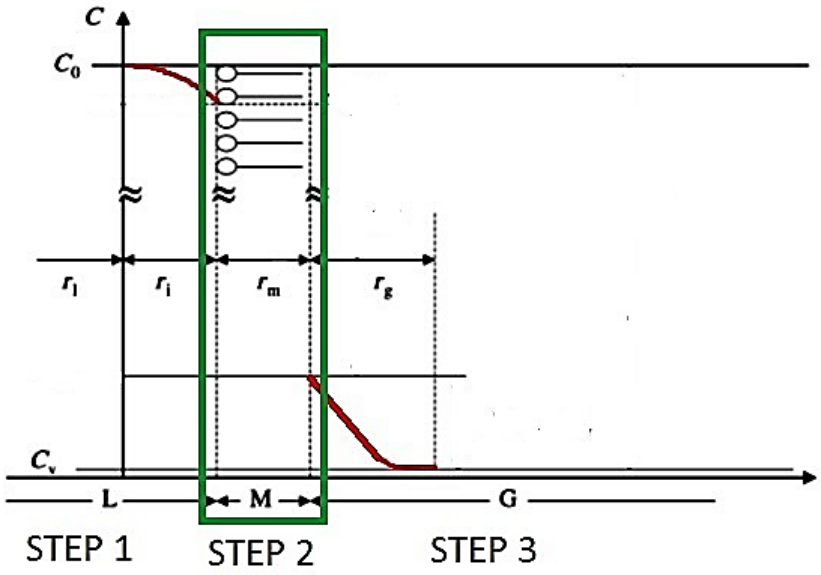



**Figure 3.15:** Schematic concentration profile of alcohol molecules from bulk aqueous solution to the gaseous phase where $r_l$, $r_i$, $r_m$ and $r_g$ are resistance of bulk aqueous phase, resistance of surfactant's layer, and resistance of the gaseous phase. L=liquid phase; M=surfactant monolayer; G = gaseous phase. $C_0$ = initial concentration of alcohol molecules in the bulk aqueous solution; $C_v$ = concentration of alcohol molecules in the gaseous phase at some distance above the liquid surface (Rusdi and Moroi, 2004).

The ability of non-ionic, anionic and cationic surfactants to retard or reduce the methanol evaporation from 24% methanol in water was evaluated in this study. Table 3.12 summarizes $K_G$ values and the percent retardation of $K_G$ of methanol obtained with the presence of SDS, CTAB and Triton X-100 as anionic, cationic and non-ionic surfactant.

**Table 3.12:** $K_G$ and percentage of $K_G$ retardation of methanol obtained by using 24% methanol in water and with the presence of CTAB, SDS and Triton X-100

| Liquid mixtures | $10^2 K_G$ (cm $s^{-1}$) | #Retardation of $K_G$ (%) |
|---|---|---|
| 0.275 mM of SDS | 53.38 ± 0.12 | 3.38 |
| 0.550 mM of SDS | 68.78 ± 0.11 | -24.49 |
| 0.825 mM of SDS | 80.34 ± 0.10 | -45.41 |
| 1.10 mM of SDS | 90.72 ± 0.09 | -64.20 |
| 0.275 mM of CTAB | 56.10 ± 0.20 | 19.60 |
| 0.550 mM of CTAB | 64.78 ± 0.19 | 7.17 |
| 0.825 mM of CTAB | 43.44 ± 0.18 | 37.75 |
| 1.10 mM of CTAB | 52.69 ± 0.17 | 24.49 |
| 0.275 mM of Triton X-100 | 29.03 ± 0.03 | 47.46 |
| 0.550 mM of Triton X-100 | 14.21 ± 0.02 | 74.28 |
| 0.825 mM of Triton X-100 | 38.71 ± 0.19 | 29.94 |
| 1.10 mM of Triton X-100 | 19.92 ± 0.20 | 63.95 |

# Retardation of $K_G$, % = [(rate coefficient for evaporation of 24 % v/v methanol - rate coefficient for evaporation of liquid mixture)/ rate coefficient for evaporation of 24 % v/v]*100

Based on $K_G$ values in Table 3.13, CTAB and TritonX-100 were found to reduce the $K_G$ value of methanol (indicated by increasing value of retardation of $K_G$ (%)) whereas SDS enhanced the $K_G$ of methanol (indicated by decreasing value of retardation of $K_G$ (%)). In order to explain the availability of the surfactant molecules at the surface of the mixture, surface tension for all the surfactant-methanol-water mixtures were measured and the results were presented in Table 3.13 and Figure 3.16. In detail, the addition of CTAB and Tritox X-100 into the selected methanol-water mixture was found to decrease the surface tension (Figure 3.16). Conversely, the surface tension measurement of 24% methanol in water does not show any significant changes with increasing SDS concentration (Figure 3.16).

**Table 3.13:** Surface tension of water-alcohol-surfactant mixtures at 303.15 K and 101325 Pa

| No. | Sample | Surface Tension (mN/m) |
|---|---|---|
| 1 | MeOH 24% | 46.68 ±0.01 |
| 2 | 0.138 mM SDS in 24% MeOH | 46.75 ±0.01 |
| 3 | 0.275 mM SDS in 24% MeOH | 46.75 ±0.01 |
| 4 | 0.550 mM SDS in 24% MeOH | 46.35 ±0.01 |
| 5 | 0.825 mM SDS in 24% MeOH | 45.65 ±0.01 |
| 6 | 1.10 M SDS in 24% MeOH | 45.93 ±0.01 |
| 7 | 0.138 mM CTAB in 24% MeOH | 46.33 ±0.01 |
| 8 | 0.275 mM CTAB in 24% MeOH | 45.93 ±0.01 |
| 9 | 0.550 mM CTAB in 24% MeOH | 44.33 ±0.06 |
| 10 | 0.825 mM CTAB in 24% MeOH | 43.05 ±0.05 |
| 11 | 1.10 mM CTAB in 24% MeOH | 42.66 ±0.05 |
| 12 | 0.138 mM TritonX-100 in 24% MeOH | 41.35 ±0.01 |
| 13 | 0.275 mM TritonX-100 in 24% MeOH | 39.75 ±0.01 |
| 14 | 0.550 mM TritonX-100 in 24% MeOH | 38.97 ±0.01 |
| 15 | 0.825 mM TritonX-100 in 24% MeOH | 35.58 ±0.01 |
| 16 | 1.10 mM TritonX-100 in 24% MeOH | 35.33 ±0.01 |

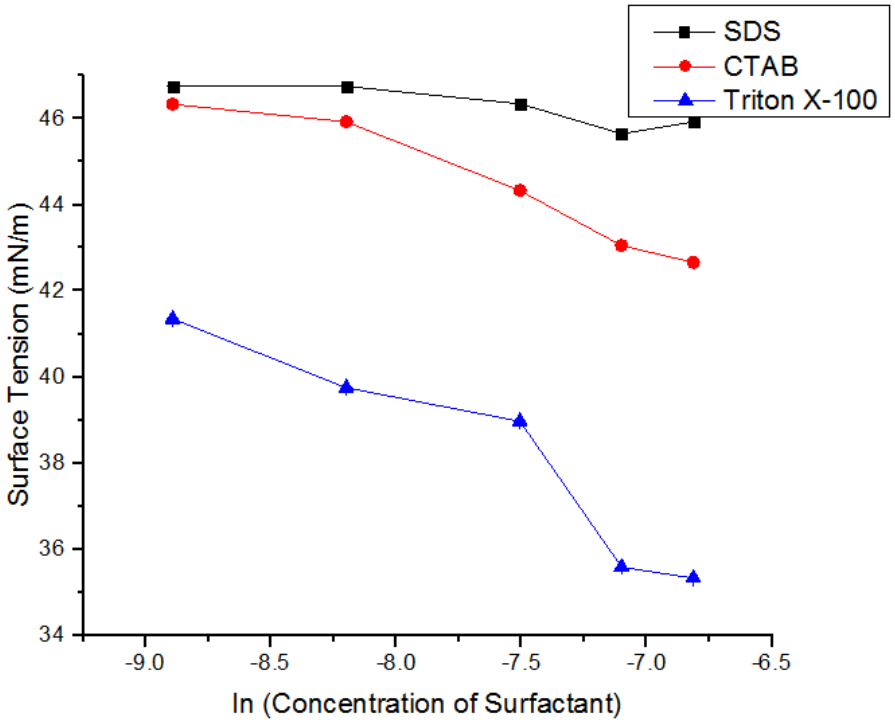



**Figure 3.16:** The plot of surface tension of versus ln (Concentration of surfactant) obtained from the surfactant-methanol-water mixtures listed in Table 3.13.

According to the result of surface tension measurement, by increasing the concentration of CTAB and Triton X-100 in the methanol-water mixture, the surfactant molecules tend to populate at the surface and decreased the surface tension of the mixture (Figure 3.16). Before any surfactant been added to the mixture, methanol molecules can act as surface active agent that tends to adsorb at the air-liquid interface and evaporate off. However, when CTAB or Triton X-100 was added to the mixture, the methanol molecules need to compete with the surfactant molecules in order to adsorb at the liquid surface. Since the tendency for the surfactant to absorb at the surface of the methanol-water mixture is higher than methanol, methanol molecules need to cross the surfactant layer for evaporation. With the presence of CTAB and Triton X-100, the $K_G$ of methanol was reduced; however no specific trend of $K_G$ variation was observed when the concentration of CTAB and Triton X-100 was increased (Table 3.12). This result might due to the selected amount of CTAB and Triton X-100 was not enough to form a uniform smooth surfactant layer which can completely cover the surface of methanol-water mixture.

For anionic surfactant, SDS, the surface tension measurement remained almost constant with increasing SDS concentration in the methanol-water mixture (Figure 3.16). This result indicated that the SDS is unlikely to adsorb at the surface of the methanol-water mixture. In this case, methanol molecules has higher tendency to adsorb at the air-liquid interface as compared to the SDS molecule. Miyata et al (1990) reported that when the SDS was dissolved in methanol, the enthalpy of the system will be increased and creating an unstable condition. This result indicated that SDS is not likely to be dissolved in methanol. Therefore, in the SDS-methanol-water mixture, when the concentration of the SDS increased, methanol molecules tend to move away from SDS by moving toward the surface of the mixture and consequently enhanced the evaporation of methanol from methanol-water mixture.

In general, the suppression of $K_G$ for 24% of methanol in water is determined by the type of surfactant being added to the mixture. Addition of surfactant such as CTAB and Triton X-100 which can form the absorbed surfactant layer at the surface of the solution will suppress the methanol evaporation. However, SDS is the least effective surfactant where it will enhance the evaporation of methanol. The effectiveness of the surfactant to retard the evaporation of methanol from methanol-water mixture is as follows:

SDS < CTAB = Triton X-100

Increasing the ability to suppress the methanol evaporation

# CHAPTER 4

# CONCLUSION

The rate of coefficient for evaporation ($K_G$) and diffusion coefficient ($D$) of methanol, ethanol, 1-propanol and 1-butanol were determined using RF-GC. The deviation of the obtained $D$ values from theoretical values calculated using Fuller-Schettlar-Giddings (FSG) model were less than 2% in all cases. This result indicated that RF-GC can be a good alternative method and instrument for the measurement of the rate of evaporation for alcohols. This method is unique because of its simplicity in the measurement of the rate of evaporation since the time taken to acquire the data is less than 3 hours. Furthermore, this method enables the measurement of $K_G$ and $D$ for the volatile liquids simultaneously.

In this work, the evaporation of alcohols with the presence of water was study in detail by focusing on the effect of water fraction, temperature and carbon number on $K_G$ and $D$ of selected alcohols. For the effect of water fraction, the result indicated that with the presence of water, $K_G$ values of methanol and ethanol were largely reduced due to the formation of hydrogen bond between water and alcohol molecules. As most of the evaporation process, the rate of evaporation of selected alcohols from alcohol-water mixtures was also found to increase with temperature. In addition, ethanol and 1-propanol were found to be more volatile than methanol and butanol for the pure alcohol liquid and even with the presence of 5% water. With the presence of 10% water, 1-propanol showed the highest $K_G$ as compared to methanol, ethanol and 1-butanol.

The effect of surfactants on the alcohol evaporation was also study in detail. The result indicated that with the presence of Triton X-100 which is a nonionic surfactant, the rate of evaporation of methanol and ethanol from the pure alcohol liquid can be largely

reduced due to the formation of insoluble surfactant layer that covered the surface of the alcohols. The effect of nonionic surfactant, anionic surfactant and cationic surfactant on the evaporation of methanol from 24% methanol in water was evaluated using Triton X-100, SDS and CTAB, respectively. The result showed that Triton X-100 and CTAB can be used to reduce the methanol evaporation. On the other hand, SDS was found to enhance the methanol evaporation from the methanol-water mixture. Generally, this study showed that nonionic and cationic surfactant can be used to reduce the evaporation of hazardous methanol from methanolic wastes.

In general, it can be concluded that RF-GC methodologies can be considered as an instrumental approach to investigate the physicochemical properties of volatile chemicals such as organic solvents at gas-liquid interface. This methodology can be used to determine the $K_G$, $D$ as well as the energy required for evaporation for low molecular weight and volatile solvents. Due to the methodology's precision, RF-GC can be further modified for future research such as to study the evaporation of hazardous solvent which may cause devastating effect to human health.

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## Publications and conference participations arising from this thesis

The work presented in this thesis has resulted in the following publications;

1. H.H. Mohammad, Sharifuddin Mohd Zain, Rashid Atta Khan, Khalisanni Khalid (2013). Study the Effect of Imposing Surfactants toward the Evaporation of Low Molecular Weight Alcohol. *International Journal of Environmental Science and Development, 4*(4), 403-407.
   (*non-ISI*/*non-SCOPUS*)

2. H.H. Mohammad, Sharifuddin Mohd Zain, Rashid Atta Khan, Khalisanni Khalid (2014). Analysis of Physicochemical Properties of Low Molecular Weight Alcohols influenced by Triton-X Monolayer(s) using Reversed Flow-Gas Chromatography (RF-GC) Technique. *Journal of Food, Agriculture & Environment* (Accepted for publication)
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**Conferences:**

| No | Event | Title of Paper Presented | Role | Start Date | End Date | Organizer | Level |
|---|---|---|---|---|---|---|---|
| 1 | 2013 2nd Journal Conference on Environmental Science and Development | Study the Effect of Imposing Surfactants toward the Evaporation of Low Molecular Weight Alcohol | Oral | 8-June-2013 | 9-June-2013 | International Journal of Environmental Science and Development | International |
| 2 | 5th UM-NUS-CU Trilateral Mini Symposium and Scientific Meeting 2014 | The Influence of Triton X-100 on the Evaporation Rate of Methanol – An analysis using Reversed Flow Gas Chromatography (RF-GC) Methodologies | Poster | 11-Feb-2014 | 12-Feb-2014 | Department of Chemistry, Faculty of Science, Universiti Malaya | International |

**Awards:**

| No | Event | Title of presentation | Achievement | Start Date | End Date | Organizer | Level |
|---|---|---|---|---|---|---|---|
| 1 | International Engineering Invention & Innovation Exhibition (i-Envex) 2014 | Poster | Bronze | 11-Apr-2014 | 13-Apr-2014 | Universiti Malaysia Perlis | International |

# Study the Effect of Imposing Surfactants toward the Evaporation of Low Molecular Weight Alcohol

Mohammad Hafiz Hamzah, Sharifuddin Mohd Zain, Rashid Atta Khan, Khalisanni Khalid

***Abstract*—In this paper, Reversed-Flow Gas Chromatography (RF-GC) is utilized to investigate the evaporation of low molecular weight alcohol. Evaporation rates as well as the diffusion rates of methanol are determined with a surfactant monolayer on the surface of the liquid; while nitrogen acts as carrier gas, at 313 K. The precision (>99.9%) and accuracy of this investigation demonstrates the potential of current methodologies for environmental impact studies; this is further verified when the results are compared with the available literature. The varying evaporation rates of methanol in the presence of varying amounts of Triton X-100 reflects that application of surfactants do damper the evaporation rates of liquid pollutants; without interference with the former's diffusion coefficients. High amounts of Triton X-100 are required for retardation of evaporation rates, suggesting the formation of a densely packed surface monolayer or the formation of an insoluble monolayer.**

***Index Terms*—Evaporation, diffusion coefficients, rate coefficients, surfactants.**

## I. Introduction

The ecological fate and evaporation of pollutant liquids are co-related to each other, especially when the compounds are introduced into both freshwater and marine environments through industrial effluents, or introduced directly into the air from industrial unit process units such as bioreactors and cooling towers [1]. The process is highly dependent on the concentration of the pollutant liquid, it will travel according to the concentration gradient, i.e. from high concentration to low concentration of the respective liquid. There are barriers that contribute to the evaporation rate [3] which includes the "stagnant" gaseous and liquid layer close to the surface, across which the vapor must diffuse. One area of application is industrial accidents, for example such as when the MV Bunga Alpinia 3 exploded while being loaded with methanol on 26 July 2012 at the PETRONAS jetty in Labuan [2]. As a result, methanol – one of the liquids under study, spilled into the sea near Labuan. The Reversed-Flow Gas Chromatography (RF-GC) method can be used as an indicator to 'measure' the evaporation rates of liquid pollutants and can quickly guide actions to be taken by the respective authorities, such as applying a suitable surfactant to curb the methanol from being evaporated into the air – this effort will help prevent the people nearby from inhaling the hazardous vapors of methanol. This may be possible if the application of surfactant on the liquid pollutant results a drastic retardation of the evaporation rate, mainly because of the presence of adsorbed monolayers [3]. Because RF-GC sampling is fast and accurate, it is a reliable method to investigate how much liquid pollutant has been evaporated into the air. Besides that, the methodologies can also embrace the area of food chemistry, chemical kinetics, catalyst and catalysis [4]. Surfactants which form monolayers at the air-liquid interface have been found to cause a significant reduction in the evaporation rate of water. Long chain alcohols decrease the evaporation rate of the water on an actual lake by a factor of 46-50% [16-22]. This paper demonstrates the utilization of RF-GC in the study of evaporation of a low molecular alcohol weight (methanol), with various amounts of the nonionic surfactant Triton X-100.

Manuscript received March 24, 2013; revised May 2, 2013. This work was supported in part by the University of Malaya under Grant RG045/09SUS.

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## II. Methodology

### A. Preparation of the TritonX-100-methanol solution

The Gibbs adsorption equation (solutions of nonionic surfactants) as stated below [5]

$$\Gamma_1 = -\frac{1}{2.303RT}\left(\frac{\partial\gamma}{\partial \log C}\right) \quad (1)$$

is used to prepare the various Triton X-100 – methanol solutions in order to determine the amount of Triton X-100 per unit area.

- $\gamma$ is the surface tension in $N.m^{-1}$ initially and then converted to $J.m^{-2}$.
- $C_1$ is the molar concentration of the surfactant at the experimental absolute temperature $T = 298.15$ K
- $R = 8.314$ J. $mol^{-1}.K^{-1}$ is the ideal gas constant
- $\Gamma_1$ is the surface excess constant of the surfactant in $mol.m^{-2}$.

The surface tension, $\gamma$ is plotted against the log of the concentration, $C_1$ to determine the surface area per molecule, $\alpha_1^s$ as shown in Fig. 1

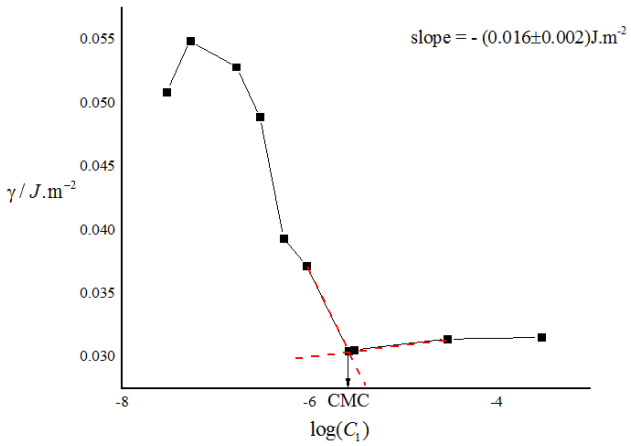


Fig. 1. Plot of the surface tension ( $\gamma$/J.m$^{-2}$) against the log of $C_1$, where $C_1$ is the bulk phase concentration of the various aqueous solutions of Triton X-100 surfactant, at 298.15 K.
**CMC = Critical micelle concentration Surface tension measurements were performed by using a Kruss Tensiometer K100.

The surface excess concentration of Triton X-100 was calculated: $\Gamma_1 = (2.78\pm0.04)10^{-6}$ mol.m$^{-2}$ by using the slope of Fig. 1. From the value $\Gamma_1$ obtained, a specific surface area per molecule at the interface was calculated as follows [6]:

$$\alpha_1^s = \frac{10^{20}}{N_A \Gamma_1} \qquad (2)$$

where $N_A$ is Avogadro's number and $\Gamma_1$ is in mol.m$^{-2}$. The value of $\alpha_1^s$ was found as (5.975±0.080).10$^{-9}$m$^2$.The values of $\Gamma_1$ and $\alpha_1^s$ were found with the same magnitude of the similar homologous head group of nonionic surfactants given on the page 78 of Ref 5. The CMC** for the aqueous solutions of Triton X-100 was found to be $C_1$ = 2.57.10$^{-4}$M or 0.0002% vol. The theoretical coverage of the Triton X-100 monolayer, ranging from 1 to 4 monolayers was determined [3], since the surface area of the bottle containing the evaporating liquid under study, $a_L$ as well as the specific surface area per molecule at the interface, $\alpha_1^s$ were known.

### B. Materials

The solutes used as evaporating liquids (stationary phase) were Merck "SupraSolv®" (methanol) and TritonX-100 (iso-Octylphenoxypolyethoxyethanol, $d$ = 1.06 g. ml$^{-1}$ and $M$ = 646.37 g.mol$^{-1}$). Purified nitrogen (99.9% purity) supplied by Malaysian Oxygen Berhad (MOX) was used as the carrier gas (mobile phase). Hydrogen and compressed air used to fuel the FID were supplied by MOX as well.

### C. Techniques

The apparatus used and the experimental procedure followed have been described elsewhere [8],[9]. A conventional gas chromatograph (Shimadzu, Series GC-14B) with a flame ionization detector (FID) and Shimadzu Solution as the software program was used for this experiment. The diffusion column (28.5 cm x 4.0 mm i.d.) was placed perpendicular to the center of the sampling column $l'$ and $l$ of [(57 + 57) cm x 4.0 mm i.d.], as shown in Figure 2. Both columns were connected by a 6.35 mm Swagelok tee union. The columns used in this chromatography were 6.35 mm diameter stainless-steel, unfilled with any solid material. All column sections were located inside the oven. The carrier gas was adjusted to a 1 cm$^3$min$^{-1}$ continuously flows through the sampling column, while it is stagnant inside the diffusion column, $L$. A glass bottle (2cm$^3$) filled with methanol (4 cm$^3$) was placed at the lower close end of the diffusion column, with a 6.35mm Swagelok stainless nut.

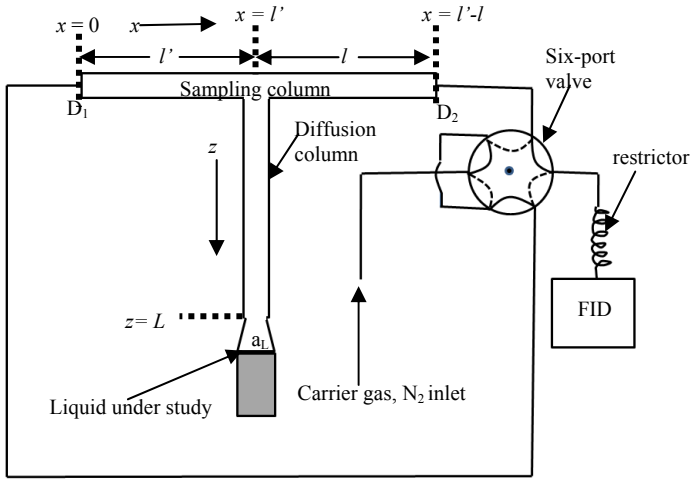


Fig. 2. The apparatus of the reversed-flow gas chromatography technique, for measuring rate coefficients and diffusion coefficients of liquids.

A six-port valve as shown in fig 2 was used to permit the carrier gas to enter either from $D_2$ and out at $D_1$ then immediately to the FID (valve position indicated by the solid line) or vice versa (the valve is switched to the dotted-line position). The valve reversed the direction of the carrier gas for 6 s, which a shorter time period than the gas's hold-up time in both column section $l'$ and $l$, then the gas was returned to its original direction, with resulting extra chromatographic peaks (sample peaks) superimposed on the continuous elution curve as depicted in fig 3.

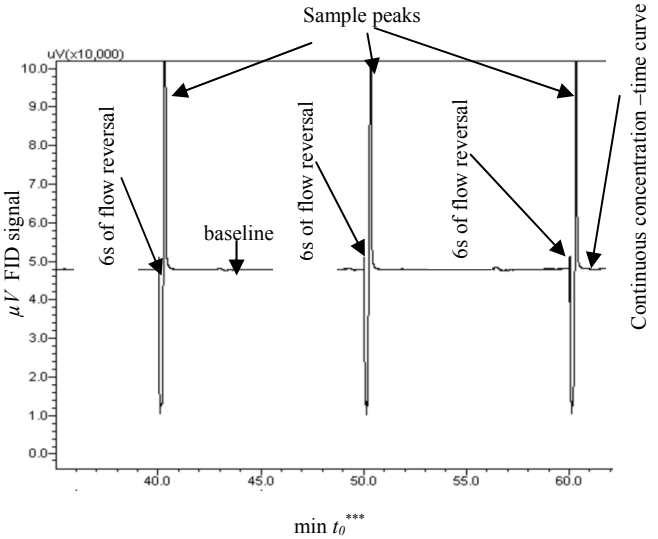


Fig. 3. A reversed flow chromatogram showing two sample peaks for the diffusion of liquid vapors into carrier gas nitrogen at 323.15 K and 101325 Pa (volumetric flow rate = 1 cm$^3$min$^{-1}$)
***$t_0$ = Time from the beginning to the last reversal of gas flow

The process was repeated during the experiment, lasting for 5 hours and 40 minutes. The pressure drop along section $l'$ and $l$ was negligible as the carrier gas flow rate was kept constant. (1.0 $cm^3 .s^{-1}$)

*D. Theoretical basis*

The height, $h$ of the sample peaks from the continuous signal, taken from baseline to the maximum, was plotted as $\ln h$ versus time, giving a *diffusion bands* as shown in Fig. 4.

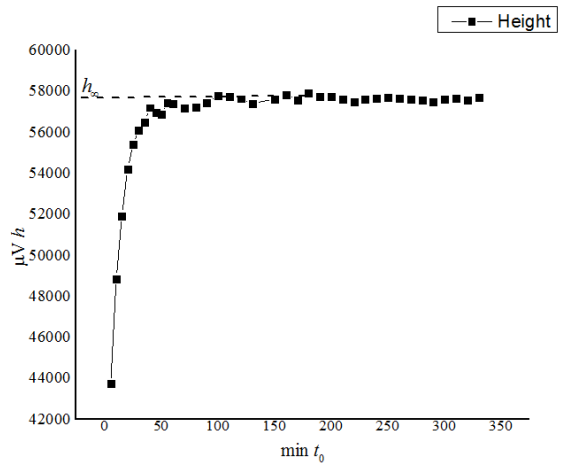


Fig. 4. Diffusion band (plot of sample peaks height, $h$, against time, $t_0$, from the beginning of the experiment) for the evaporation of liquid, at 313.15 K and 101325 Pa.

Each sample peak which has been shown earlier [8], produced by two reversals in RF-GC, is symmetrical and its maximum height $h$ from the ending baseline is given by

$$h \cong 2c(l', t_0) \tag{3}$$

Thus, the concentration of the vapors of an evaporating liquid, $c(l', t_0)$ at $x = l'$ and time $t_0$ is proportional to the height or the area of the experimentally obtained sampling peaks, and it is interrelated with the rate coefficient for the evaporation process, $K_G$, the diffusion coefficient of the vapor into the carrier gas, $D$, and the geometrical details of the diffusion column through the relation [8]:

$$c(l', t_0) = \frac{K_G D c_0}{V(K_G L + D)} \left\{ 1 - \exp\left[ -2(K_G L + D) t_0 / L^2 \right] \right\} \tag{4}$$

where $L$ is the length of the diffusion column and $v$ the volumetric flow rate of the carrier-gas. Figure 5 represents the sampling of the above-mentioned process against time. It becomes obvious that after a period of time, which is characteristic of each particular interaction system, a steady-state situation is achieved. From this plot, at long times an infinite value for the peak height $h_\infty$ can be obtained. This infinity $h_\infty$ value is used for the linearization of the resulting relation [8]:

$$h_\infty = \frac{2K_G D c_0}{\left[ v(K_G L + D) \right]} \tag{5}$$

Using the former approximation, one obtains [8]:

$$\ln(h_\infty - h) = \ln h_\infty - \left[ \frac{2(K_G L + D)}{L^2} \right] t_0 \tag{6}$$

Thus, at long enough times, for which Eq. 4 was derived,a plot of $\ln(h_\infty - h)$ vs. $t_0$ is expected to be linear, and from its slope $-2(K_G L + D)/L^2$ a first value of $K_G$ can be calculated from the known value of $L$ and a literature or theoretically calculated value of $D$. [9] – [11]

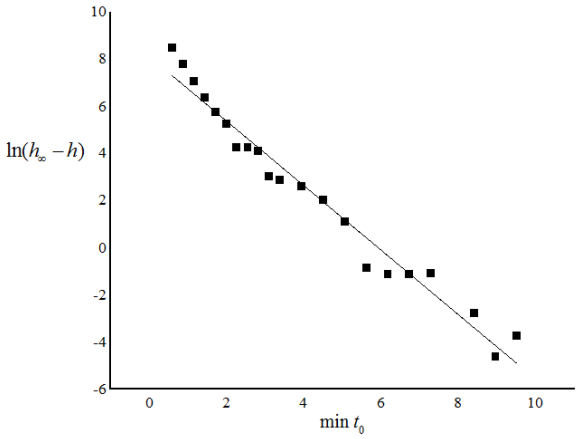


Fig. 5. Example of plot for the diffusion of liquid vapor into carrier gas at 313.15 K and 101325 Pa ($v$ = 1.00 $cm^3 s^{-1}$)

The value of $K_G$ can now be used to plot small time period data according to Eq. 14 of Ref. 9, which is substituted now for $c(l', t_0)$ in Eq. 2. After rearrangement, logarithms are taken and there results:

$$\ln\left[ \left( \frac{L}{2t_0^{\frac{1}{2}}} + K_G t_0^{\frac{1}{2}} \right) \right] = \ln\left[ \frac{4K_G c_0}{v} \left( \frac{DL}{\pi} \right)^{\frac{1}{2}} \right] - \frac{L^2}{4D} \frac{1}{t_0} \tag{7}$$

Now a plot of the lefthand side of this relation versus $\frac{1}{t_0}$ will yield a first approximation experimental value for $D$ from the slope $\frac{-L^2}{4D}$ of this new linear plot

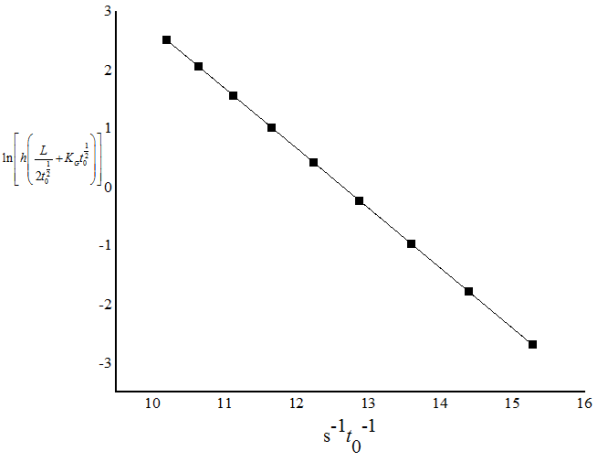


Fig. 6. Data from evaporation of liquid vapor into carrier gas at 323.15 K and 101325 Pa ( $v$ = 1.00 $cm^3$ $sec^{-1}$), plotting according to Equation 7

## III. Results and Discussion

TABLE I: Rate Coefficients for the Evaporation of Methanol, $K_G$, and Diffusion Coefficients of Its Vapors Into Nitrogen, $D_{FOUND}$, Under the Effect of Various Amount of Surfactant Triton X-100, at 313.15 and 101 325 Pa

| Monolayer Thickness of Triton X-100 | $10^2K_G$ (cm $s^{-1}$) | Retardation of $k_c$, % | $10^3D_{found}$ /$cm^2s^{-1}$ | $10^3D_{lit}$/$cm^2s^{-1}$ | $10^3D_{lit}$/$cm^2s^{-1}$ | Deviation,% | Deviation,% |
|---|---|---|---|---|---|---|---|
| 0 | 96.69 ± 0.20 | - | 181.8 ± 0.04[a] | 184.31 | 200.58 | 1.4[*] | 9.3[#] |
| 1 | 31.75 ± 0.05 | 67.2 | 189.23 ± 0.02[a] | 184.31 | 200.58 | 2.6[*] | 5.7[#] |
| 2 | 20.71 ± 0.14 | 78.6 | 188.07 ± 0.02[a] | 184.31 | 200.58 | 2.0[*] | 6.2[#] |
| 3 | 17.31 ± 0.07 | 82.1 | 183.14 ± 0.02[a] | 184.31 | 200.58 | 0.6[*] | 8.7[#] |
| 4 | 12.30 ± 0.31 | 87.3 | 189.46 ± 0.02 | 184.31 | 200.58 | 2.7[*] | 5.5[#] |
| | Mean values | | 186.35 ± 0.02 | | | (1.9[*])[c] | (7.1[#])[c] |
| | Precision, % | | 99.9[b] | | | | |

[a]Uncertainty obtained from the standard error of the $k_c$ and $D$ values, estimated from the slopes of the linear plots of Eqs. 20 and 21 of Ref. 8 respectively.
[b]Precision determined from the mean value and the standard error of the experimentally obtained diffusion coefficients.
[c]Mean deviation of the experimental diffusion coefficients from the respective predicted[*][11] and experimental[#][15] literature values, $D_{lit}$.

Table I summarizes the results for the evaporation of methanol under the influence of the surfactant Triton X-100 ranging from 0 to 4 monolayers. The diffusion coefficients which are determined from this experiment were compared with the predicted values from the Fuller-Giddings equation [11] and experimentally obtained values from previous experimental work [15] which was using a different method. The deviation of the diffusion coefficients of the current experiment from the predicted and experimental literature values, $D_{lit}$ are illustrated in the last column and are based on the following equation:

$$Deviation(\%) = [\frac{(D_{found} - D_{theoretical/literature})}{D_{found}}] \text{x} 100$$

Based on the diffusion coefficient values, $D_{found}$, ones can be assured that they are independent of the addition of surfactant, as expected [3]. The mean deviation of the methanol + Triton X-100 liquid mixtures experimental obtained by RF-GC, $D_{found}$, from the predicted and literature values are 1.9 and 7.1 % respectively. The $D_{found}$ values falls between the predicted and literature ones. The total reproducibility of this method is determined 99.9% for the case of the liquid stated.

The uncertainty in the determination of the vaporization values, $k_c$, varies from 0.2 to 2.5% in this case. Based on the percentages, we can conclude that the values experimentally obtained by use of RF-GC can be used to reliably predict the effect of Triton X-100 in the evaporation rates of methanol.

We can conclude that the $k_c$ values in the presence of various amounts of Triton X-100 corresponding to the formation of an adsorbed monolayer at the surface of the methanol; demonstrating that Triton X-100 does make the evaporation rates decrease. The evaporation rate retards by a high percentage, i.e. 67.2%; with just one monolayer of TritonX-100 being applied on the surface of the methanol.

## IV. Conclusion

The present method gives an alternative from the previous method [15], since the former method can be used in simultaneously determining the evaporation rates and diffusion rates of the liquid under study. The present method can be considered accurate since the results show that the diffusion in the current experiment deviates from the predicted theoretical value by less than 2.0% (based on mean values); as compared from the works by Anikar H.J. et. al. [15]. Also, the use of RF-GC has value because of its precision and experimental simplicity.

The evaporation rates found by the current experiment are absolute and as a result they can be related to the physical properties of the evaporating species.

We can obviously extend the use of RF-GC to other topics that are related to the environmental, such as investigation of water evaporation (sea, lake, river), the effect of ionic and zwitterionic surfactants on the evaporation rates of liquid pollutants; as well as experiments with surfactants under steering conditions in order to investigate their durability[3].

## Acknowledgments

The author is indebted to the University of Malaya which supported this research project. The author wants to dedicate special thanks to Dr. Tay Kheng Soo for his critique and review of the findings from the experiments; as well as to the staff of the Department of Chemistry, University of Malaya, for their technical support. The author is also indebted to Miss Kumuthini A/P Chandrasekaram for her assistance on tensiometer usage.

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He has experienced on teaching secondary school for a year before deciding to continue his studies in area of chemistry. Mr. Hamzah is also one of the recipients of fellowship from University Malaya under the "Skim Biasiswazah", the prestigious fellowship given by the university to undergraduate student to pursue higher degree.

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Upon study, he was appointed as residential assistance for PERMATAPintar Program in Universiti Kebangsaan Malaysia. He flew away to Thailand and Singapore to give the speech on his research. His diligence was rewarded with a degree in Master of Science in Physical/ Environmental Sciences in 2011. Before graduation, he was offered to join Malaysian Agricultural Research and Development Institute (MARDI). There onwards, his interest of research in science and business grew. This was further encouraged by the recognition and support from MARDI, where he was appointed as Technical Officer for MARDI Kuala Linggi Incubator Program. This project leads him to train SMEs for essential oil production. In MARDI Headquarters Serdang, he is responsible to lead Essential Oil Analysis Unit under Food and Agricultural Analysis Laboratory Program, Technical Service Centre. He is also the gatekeeper for Malaysian Herbal Authentication Centre (MHAC).

Mr. Khalid has exposed over 5 years in diverse research areas especially research ethics, essential oil, polymer, biofuel, fermentation, analytical and environmental chemistry. He has been honoured and recognised both nationally and internationally for his research creativity and innovativeness. At his age of 28, he has published more than 60 articles in books, book chapters, and proceedings of which more than 30 articles in refereed journals.

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## Journal of Food, Agriculture & Environment – JFAE www.world-food.net

Print ISSN:1459-0255
Online ISSN: 1459-0263

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**Online ISSN:** 1459-0263 **Print ISSN:** *1459-0255*

Journal of Food, Agriculture & Environment – JFAE

## Letter of Acceptance 30.1.2014

**Ref#296**

**Analysis of Physicochemical Properties of Low Molecular Weight Alcohols influenced by Triton-X Monolayer(s) using Reversed Flow-Gas Chromatography (RF-GC) Technique**

Mohammad Hafiz Hamzah[1], Sharifuddin Mohd Zain[1], Rashid Atta Khan[1], Khalisanni Khalid[1,2,*]

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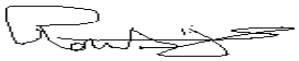

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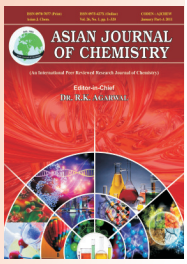
Asian Journal of Chemistry; Vol. 26, No. 23 (2014), 7871-7876

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16693




*REVIEW*

# Transport Phenomena and Evaporation on Interface of Gas-Liquid by Reversed-Flow Gas Chromatography

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*Received*: 14 November 2013; *Accepted*: 4 April 2014; *Published online*: 15 November 2014; AJC-16254

Gas-liquid interface plays a major interest in environmental studies especially when the researchers are interested to study the diffusion coefficients and rate coefficients of the liquid under studies into the chosen carrier gas. The study of the gas-liquid interface by reversed-flow gas chromatography (RF-GC) is based on Ficks first law in one dimensional and Henry's law. Based on the two laws, an extensive works have been done previously by using reversed-flow gas chromatography methodologies to determine physiochemical properties on the gas-liquid interface. The setup for this method is just by modifying the commercial gas chromatography by including diffusion column which orientated right angle to the sampling which carried the carrier gas. The bottom part consists of the glass bottle which holds the liquid under studies. The usage of six-port or four-port valves play a major role in this methodologies since the equipment allows the carrier gas to reverse and retain its original flow from time to time and thus creating a 'sample peak' which sits on the continuous signal *versus* time chromatogram. The diffusion column which contains stagnant carrier gas accounts for the stationary phase and thus contributes to the physiochemicals phenomena of the interface. This methodology can be considered as fast sampling procedure as compared to the others in term of determining rate coefficients and diffusion coefficients of liquid sample into the carrier gas. The methods not only important in environmental investigation but can also be applied in the area of material science, food chemistry, nanotechnology, biological science and chemical technology.

**Keywords: Diffusion coefficients, Fuller-shettlar-giddings equation, Gas-liquid interphase, Reversed-flow gas chromatography.**

## INTRODUCTION

Reversed-flow gas chromatography (RF-GC) is different from conventional gas chromatography essentially because it consists of sampling cell, which is composed of sampling and diffusion columns. The carrier gas flows continuously through sampling column while it remains stagnant in the diffusion column. A part or whole of diffusion column can be filled with solid or liquid substance under study[1,3-12]. The authors will limit this review up to the application of RF-GC towards the interface of gas-liquid since the review on the other interface has been extensively describe by the previous review[1]. The transport phenomena across the gas-liquid for RF-GC methodologies much concern on the diffusion of respective solute into the carrier gas. Thus, the first part of this manuscript will try to explore the works done by previous researcher on determination of the diffusion coefficients on the liquid-gas interface. Next, the author explain in the great details on the experimental set up for the determination of the diffusion rates and coefficient rates of liquid under studies with the application of surfactant monolayer at the liquid-gas interface which part of the author's current work[46]. Finally, the author will discuss the modification done on the lower part of the diffusion column of the RF-GC to calculate other physico-chemical measurements within the gas-liquid interface.

**Diffusion of gases in liquids:** Most of the methods used in the early measurement of diffusion coefficients of the liquid systems were based on static bulk equilibration methods (*e.g.*, gravimetric sorption/desorption)[1]. The limitation of this method is that it relies on the sorption and bulk equilibration which cannot be applied to solute-solvent system if the solute presents in a minute amounts. As a consequence, the time for sorption may be large because the diffusion coefficient may be small. But, the accuracy of this method may be declined due the small amount of the solute presents.

**Evaporation of liquids:** Evaporation is a process which converting a substance which in the liquid phase into the vapor phase. The process must overcome the strong forces of

attraction between the molecules, which are balanced equally strong forces of repulsion. Thus, in order to overcome the potential energy of attraction, the molecules require kinetic energy which is a function of temperature. The molecules obeys the following equation if the process occurs at the constant volume[2],

$$\frac{n_v}{n_l} = e^{\frac{\Delta E}{RT}} \quad (1)$$

where $n_v$ is the number of molecules per milliliter in the vapor, $n_l$ is the number of molecules per milliliter in the liquid, $\Delta E$ is the difference in molar internal energy of the gas and liquid, R is the gas constant and T is the absolute temperature.

When the molecules gain the kinetic energy, they will evaporate from the liquid which results the average kinetic energy of the remaining molecules decreases. This can be observed as the temperature drops at the beginning of the process. Thus, heat must be released to the liquid in order to maintain the temperature. Realistically, the evaporation process occurs at constant pressure which differs from the prediction that it occurs at the constant volume. Thus, ones can relate the evaporation process with the first law of thermodynamic by the relation[2]:

$$\Delta H = \Delta E + P\Delta V \quad (2)$$

where $P\Delta V$, portrays the work done by vapor at constant atmospheric pressure which result in volume expansion. Thus, $\Delta H$ can be describe as the energy required to evaporate one mole of liquid at constant pressure, or simply called the molar heat of vaporization.

Since the gas obeys the ideal gas law to the first approximation ($PV = RT$)[2], thus the relation gives the latent heat of vaporization:

$$\Delta H = \Delta E - RT \quad (3)$$

$\Delta H$ is a function of temperature is usually measured by calorimeter at the normal boiling point.

The factors that affecting the rate of evaporation of a liquid are as follow: (i) Concentration of the substance evaporating in the air, (ii) Concentration of the other substances in the air, (iii) Concentration of the other substances in the liquid (impurities), (iv) Flow rate of air just above the liquid surface, (v) Inter-molecular forces (attractive-repulsive) between the molecule of the liquid, (vi) Pressure at the surface of the liquid, (vii) Surface area of the liquid that is being exposed, (viii) Temperature of the liquid, (ix) Density of the liquid, (x) Monolayer thickness that being applied at the gas liquid interface, (xi) Intermolecular interference on the surface of liquid bodies.

**General principle of reversed-flow gas chromatography:** The technique of reversed-flow gas chromatography was first introduced by Prof. N.A. Katsanos and his co-workers at the Laboratory of Physical Chemistry, University of Patras, Athens, Greece[3-16]. In the recent review of the reversed-flow gas chromatography[17], the author did mention that RF-GC is first proposed for kinetic studies heterogenous catalysis[18] and then the method is applied to the dehydration of alcohols and the deamination of primary amines[17-19]. Many publications using this technique have been published, this may include the determination of gas diffusion coefficients in binary and ternary gas mixture[5-8], determination of adsorption equilibrium constant[9], determination of rate constants, activation parameters as well as determination of catalytic conversion of reactants into products for various important surface catalyzed reactions[13-15,20] and determination of Flory-Huggins interaction parameters and solubility parameters in polymer-solvent system[16]. Besides that, RF-GC also plays an important role in determination of rate coefficients for evaporation of liquids[21], determination of mass transfer and partition coefficients across gas-liquid and gas-solid interfaces[22-25] and in determination of adsoption energies, local monolayer capacities and local adsorption isotherms[26,27]. Furthermore RF-GC also has being used in determination of rate constant for sorption of various gases on bimetallic catalyst[28,29] and in determination of activity coefficient[20]. As far as the author concerns, RF-GC has been used to study the evaporation of the pollutant liquids under the influences of the surfactant[30] as well as the vigorous works from our laboratory which measure the diffusion rates, coefficients rates and activation energy of pure liquid pollutants[31-39] can be considered as the latest publication under this area.

Reversed-flow gas chromatography is just another sampling technique that manipulates the flow of the carrier gas by reversing the flow at regular time interval with the assistance of four or six-port valve. The process can be done manually or using automatic four or six valve with suitable computer programming. Each flow reversal will produce flow perturbation on the chromatographic elution curve by having extra peaks, or will be considered as "sampling peaks" in the rest of this article as shown in the Fig. 1.

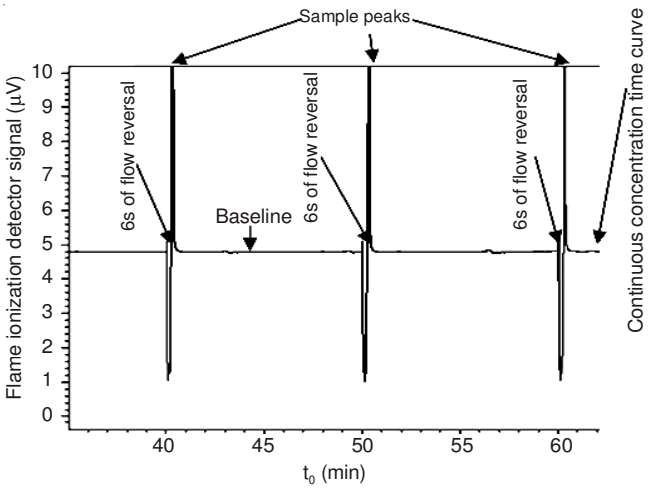


Fig. 1. Reversed flow chromatogram showing three sample peaks for the diffusion of liquid pollutant vapors into carrier gas nitrogen at 313.15 K and 101.325 kPa (volumetric flow rate, v = 1 $cm^3 min^{-1}$)

## EXPERIMENTAL

**Experimental arrangement of the reversed-flow gas chromatography consists of the following parts:**

(1) A commercial gas chromatography with any kind of detector. Flame ionization detector (FID) is highly recommended due to its sensitiveness.

(2) A sampling column which is made of unfilled stainless steel chromatographic tube of ¼ inch in diameter and having total length of 0.8-2.5 m depending on the application.

(3) A diffusion column which is made from the same material as sampling column and oriented at right angle to the latter and usually at its middle point. The diffusion column is normally straight and relative short about 25-100 cm. Sampling column and diffusion column can be regarded as sampling cell and this experiment, they are placed inside the oven.

(4) Sampling cell is connected to the gas inlet on one end and the detector at the other end. The connection is such way that the carrier gas flow through the sampling column (carrier gas remain stationary inside the diffusion column) can be reversed in direction at any time interval. This possible because of the existence of six port valve that connect the ends $D_1$ and $D_2$ of the sampling column to the carrier gas supply and detector as shown in the Fig. 2.

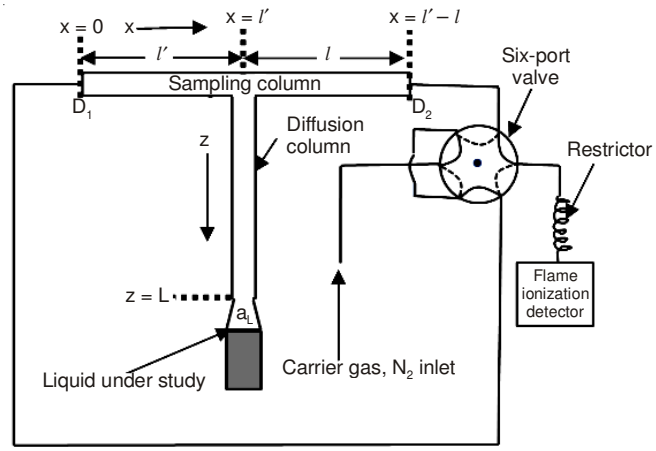


Fig. 2. Apparatus of the reversed-flow gas chromatography technique, for measuring rate coefficients and diffusion coefficients of liquids

The solid line indicates the position in which the valve is currently regulated and allowed the carrier gas to enter the column *via* $D_2$ and leave at $D_1$ toward the FID. Now, by switching the valve (indicates by the dashed line), the carrier gas direction is reversed, entering now the column *via* $D_1$.

(5) A restrictor is placed before the detector to avoid the flame of FID from being extinguished when the valve is turned from one position to other.

## MATHEMATICAL MODEL

The elution curves is described which follow the carrier gas reversal based on the common chromatographic sampling equation shows below[21]:

$$c = c_1(l', t_0 + t' + \tau)\, u(\tau) + c_2(l', t_0 + t' + \tau)[1 - u(\tau - t')] \times [u(\tau) - u(\tau - t'_M)] + c_3(l', t_0 - t' + \tau)\, u(t_0 + \tau - t')\{u(t - t') [1 - u(\tau - t'_M)] - u(\tau - t')[u(\tau) - u(\tau - t'_M)]\} \quad (4)$$

where c is concentration of vapor at detector, $c_1(l', ...)$, $c_2(l', ...)$ and $c_3(l', ...)$ are concentration at the point $x = l'$ (*cf* Fig. 1) for the times shown ($t_0$ is the total time from placing the liquid in column to the last backward reversal of gas flow, $t'$ = time interval of backward flow, $\tau$ is the $t - t_M$, t being the time from the last restoration of the carrier gas flow and $t_M$ and is the gas hold-up time of column section l: Finally the various u 's are unit step functions for the arguments shown in parentheses and $t'_M$ is the gas hold-up time in the section $l'$.

For $t'$ smaller than both $t_M$ and $t'_M$, each sample peak produced by two successive reversals which is symmetrical and its maximum height h from the ending baseline is given by[21,47]:

$$h \cong 2c(l', t_0) \quad (5)$$

where $c(l', t_0)$ is the vapor concentration at $x = l'$, time $t_0$. The concentration of the liquid can be found from the diffusion equation in the column L (Fig. 1)[21,47]:

$$\frac{\partial c_z}{\partial t_0} = D\frac{\partial^2 c_z}{\partial z^2} \quad (6)$$

where D is the diffusion coefficient of the vapor into the carrier gas. The solution of (6) is sought under the initial condition[21,47]:

$$c_z(z, 0) = 0 \quad (7)$$

As the boundary condition at z = L:

$$cz(L, t_0) = c(l, t_0) \quad (8)$$

and thus,

$$-D\left(\frac{\partial c_z}{\partial z}\right)_{z=L} = vc(l', t_0) \quad (9)$$

where $\nu$ is the linear velocity of carrier gas and the boundary condition at z = 0:

$$-D\left(\frac{\partial c_z}{\partial z}\right)_{z=0} = k_c(c_0 - c_z(0)) \quad (10)$$

where $c_z(0)$ is the actual concentration at the liquid interface at time $t_0$, $c_0$ the concentration of the vapor which would be in equilibrium with the bulk liquid phase and $k_c$ a rate coefficient for the evaporation process. Eqn. 10 expresses the equality of the diffusion flux for the removal of vapors from the liquid surface and the evaporation flux due to departure of $c_z$ at the surface from the equilibrium value $c_0$.

When the Laplace transform of (6) taken with respect to $t_0$, a linear second-order differential equation results. It can be solved by using z Laplace transformation yielding[21,47]:

$$C_z = C_z(0)\cos qz + \frac{C'_z(0)}{q}\sin qz \quad (11)$$

where

$$q = \sqrt{\left(\frac{p_0}{D_0}\right)} \quad (12)$$

and $C_z(0)$ and $C'_z(0)$ are the $t_0$ Laplace transform of $c_z(0)$ and respectively. If one combines (11) with the $t_0$ transforms of the boundary condition (8), (9) and (10), the Laplace transform of $c(l', t_0)$, denoted as $C(l', p_0)$, is found by:

$$C(l', p_0) = \frac{k_c c_0}{p_0}\frac{1}{\left(D_q + \frac{vk_c}{D_q}\right)\sin h\, qL + (v + k_c)\cos h\, qL} \quad (13)$$

The application of inverse Laplace transformation of this equation to find $c(l', t_0)$ is difficult. Thus, it can be achieved by using certain approximation which are different for small or for long times. In the first case qL is large, allowing both $\sin h\, qL$ and to be approximated by $\exp\left(\frac{qL}{2}\right)$. Then (13) becomes:

$$C(l', p_0) = \frac{k_c c_0}{p_0 Dq} \frac{2 \exp(-qL)}{\left(1 - \frac{k_c}{Dq}\right)\left(1 + \frac{\nu}{Dq}\right)} \quad (14)$$

For high enough flow rates, the equation further reduces to[21,47]:

$$C(l', p_0) = \frac{2k_c c_0}{\nu D} \frac{\exp(-qL)}{q\left(q + \frac{k_c}{D}\right)} \quad (15)$$

Taking now the inverse Laplace transform of this equation, one finds:

$$C(l', t_0) = \frac{2k_c c_0}{\nu} \exp\left[\frac{k_c L}{D} + \frac{k_c 2t_0}{D}\right] \operatorname{erfc}\left[\frac{L}{2\sqrt{(Dt_0)}} + \sqrt{(t_0)}\right] \quad (16)$$

Finally, if one uses the relation $\operatorname{erfc}(x) = \frac{\exp(-x^2)}{\left(\tau\pi^{\frac{1}{2}}\right)}$, which is good approximation[48] for large values of x, equation (16) becomes[21,47]:

$$C(l', t_0) = \frac{2k_c c_0}{\nu} \left[\frac{(D)}{\pi}\right]^{\frac{1}{2}} \exp\left[\frac{-L^2}{4Dt_0}\right] \left[\frac{L}{2t_0^{\frac{1}{2}}} + k_c t_0^{\frac{1}{2}}\right] \quad (17)$$

Coming now to the other extreme, *i.e.*, long time approximation[21,47], qL is small and the functions sinh qL and cosh qL of eqn. 13 can be expanded in McLaurin series, retaining the first three terms in each of them. Then, from eqn. 13 one obtains:

$$C(l', p_0) = \frac{k_c c_0}{p_0} \frac{1}{\left(Dq + \frac{\nu k_c}{D_q}\right) qL + (\nu + k_c)\left(1 + \frac{q^2 L^2}{2}\right)} \quad (18)$$

and by using equation (12) and rearranging this becomes:

$$C(l', p_0) = \frac{k_c c_0}{Lp_0} \frac{1}{p_0\left[1 + (\nu + k_c)\frac{L}{2D}\right] + \frac{\nu k_c}{D} + \frac{(\nu + k_c)}{L}} \quad (19)$$

For high enough flow rates $k_c$ can be neglected compared to ν and *l* can be neglected in comparison[21,47] with $\frac{\nu L}{2D}$. For instance, in a usual experimental situation it was calculated that $\frac{\nu L}{2D} = 420$. Adopting these approximations, eqn. 19 reduces, after some rearrangement, to:

$$C(l', p_0) = \frac{2k_c D c_0}{\nu L^2 p_0} \frac{1}{p_0 + \frac{2(k_c L + D)}{D}} \quad (20)$$

Finally, inverse Laplace transformation[49] of this relation yields:

$$C(l', t_0) = \frac{kDc_0}{\nu(k_c L + D)} \left\{1 - \exp\left[\frac{-2(k_c L + D)t_0}{L^2}\right]\right\} \quad (21)$$

By considering maximum height h of the sample peaks in eqn. 5 and substituting in it, the right hand side of eqn. 21 for $c(l', t_0)$ one obtain h as an explicit function of time $t_0$. In order to linearize the resulting relation, an infinity value $h_\infty$ for the peak height is required[21,47]:

$$h_\infty = \frac{2k_c D c_0}{[\nu(k_c L + D)]} \quad (22)$$

Using this expression, we obtain

$$\ln(h_\infty - h) = \ln h_\infty - \left[\frac{2(k_c L + D)}{L^2}\right] t_0 \quad (23)$$

Thus, the long enough times, for which (21) was derived, a plot of $\ln(h_\infty - h)$ *versus* $t_0$ is expected to be linear[21,47] and from the slope $\frac{-2(k_c L + D)}{L^2}$ a first approximate value of $k_c$ can be calculated from the known value of L and a literature or theoretically calculated value of D[21,47] (Fig. 3).

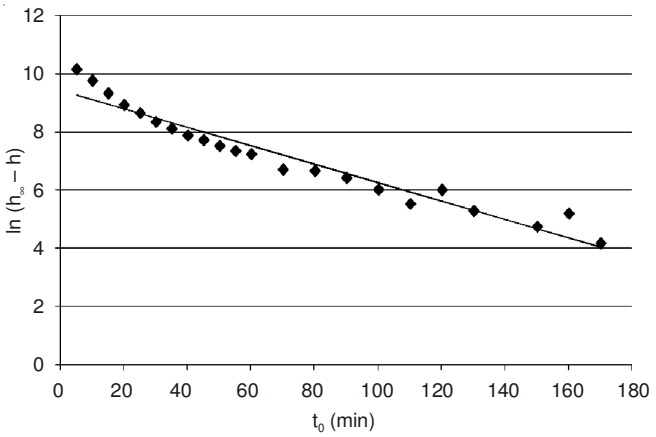


Fig. 3. Example of plotting eqn. 23 for the diffusion of liquid vapor into carrier gas at 313.15 K and 101.325 kPa. (ν = 1 $cm^3$ $sec^{-1}$)

This value of $k_c$ can now be used to plot small time data according to (17) which is substituted now for $c(l', t_0)$ in (5). After rearrangement logarithms are taken and there results[21,47]:

$$\ln\left[h\left(\frac{L}{2t_0^{\frac{1}{2}}} + k_c t_0^{\frac{1}{2}}\right)\right] = \ln\left[\frac{4k_c c_0}{\nu\left(\frac{D}{\pi}\right)^{\frac{1}{2}}}\right] - \left(\frac{L^2}{4D}\right)\left(\frac{1}{t_0}\right) \quad (24)$$

Now, a plot of the left hand side of this relation $\frac{1}{t_0}$ will yield a first approximation of experimental value for D from the slope $\frac{-L^2}{4D}$ of this new linear plot as shown in Fig. 4.

**Preparation of the liquid for studying the effect of surfactant towards the diffusion rates and coefficient rates of the low molecular weight alcohol:** The solutes used as evaporating liquids (stationary phase) were Merck alcohol and surfactant. The gases purchased from MOX (Malaysia) comprised of the carrier gas which was nitrogen of 99.99 %

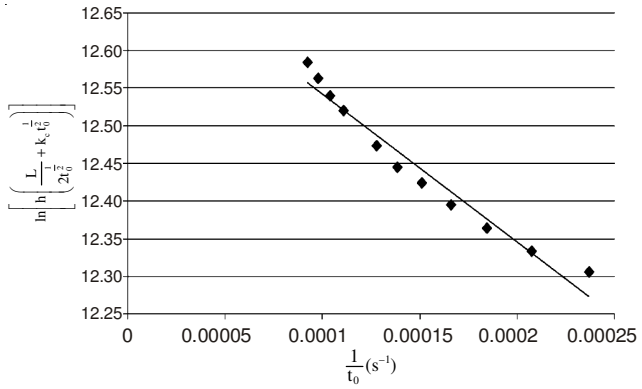


Fig. 4. Example of data from evaporation liquid vapor into carrier gas at 313.15 k and 101.325 kPa. ($\nu$ = 1 cm$^3$ sec$^{-1}$), plotting according to eqn. 24

purity as well as the fuel gases for flame ionization detector, FID which were hydrogen of 99.99 % purity and compressed air.

**Preparation of surfactant-alcohol solution:** The Gibbs adsorption equation for solutions of nonionic surfactants[40]

$$\Gamma_1 = -\frac{1}{1.303\ RT}\left(\frac{\partial\gamma}{\partial \log C}\right) \quad (25)$$

is used to prepare the various surfactant-alcohol solutions in order to determine the amount of surfactant per unit area. $\gamma$ is the surface tension in N m$^{-1}$ initially and then converted to J m$^{-2}$. $C_1$ is the molar concentration of the surfactant at the experiment absolute temperature T = 298.15 K, R = 8.314 J mol$^{-1}$ K$^{-1}$ is ideal gas constant and $\Gamma_1$ is the surface excess constant of the surfactant in mol m$^{-2}$. The surface tension, $\gamma$ is plotted against the log of the concentration, $C_1$ to determine the surface area per molecule, $\alpha_1^s$ as shown in Fig. 5.

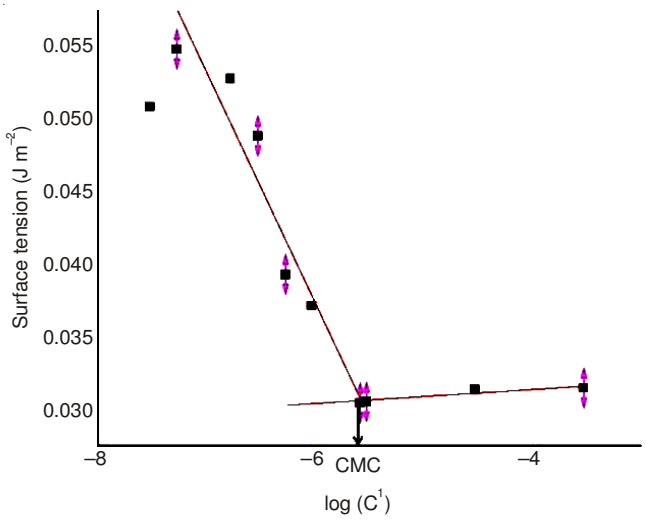


Fig. 5. Plot of the surface tension ($\gamma$/J m$^{-2}$) against the log of $C_1$, where is the bulk phase concentration of the various aqueous solution of surfactant, at 298.15 K. **CMC = Critical micelle concentration

Surface tension measurements were performed by using Tensiometer K100 by Kruss. The surface excess concentration of Tsurfactant, $\Gamma_1$ is calculated by using slope of the Fig. 5. From the value $\Gamma_1$ obtained, specific surface area per molecule at the interface is calculated as follow[40]:

$$\alpha_1^s = \frac{10^{20}}{N_A \Gamma_1} \quad (26)$$

where $N_A$ is the Avogadro's number while $\Gamma_1$ is in mol m$^{-2}$. The values $\Gamma_1$ of and $\alpha_1^s$ foundare then compared with the values of the similar homologous head group of nonionic surfactants given on the page in[39] to ensure that the values are at the same magnitude with the literature. Then, based on the theoretical coverage of surfactant monolayer, 1 monolayer is determine[40] because the correlation of the surface area of the bottle containing the evaporating liquid under study, $a_L$ as well as the specific surface area per molecule at the interface, are known. The additional monolayer is added on top of the previous added monolayer carefully by using a micrometer syringe or micropipette[41] to make 2 × monolayer. The procedure is repeated for the 3 × monolayer and 4 × monolayer.

**Other experiment considering gas-liquid interface by RF-GC:** The interface of the gas-liquid contributes to the gaseous pollutant(s) between the atmospheric and water environment[23]. Since the phenomena employs a great significance towards the environment chemistry[42], the researchers must be defined about the research that they want to explore whether to study the solubilities of air pollutant in water or the ability of the liquid pollutant to migrate from water to environment. For example, dimethyl sulfide contributes as a major source of sulfur in troposphere since the pollutant is emitted by oceanic phytoplankton[43]. The following physiochemical quantities can be calculated when ones considered the mechanism involving in the above phenomena[43]: (i) Diffusion coefficient of the pollutant in the carrier gas ($D_z$, cm$^2$/sec), (ii) Diffusion coefficient of the pollutant in the water ($D_L$, cm$^2$/sec), (iii) Partition coefficient of the pollutant between the water at the interface and the carrier gas (K, dimensionless), (iv) Partition coefficient of the pollutant between the bulk water and the carrier gas (K', dimensionless), (v) Partition coefficient of the pollutant between the water at the interface and the bulk (K", dimensionless), (vi) Henry's law constant for the dissolution of the pollutant in the water ($H^+$, atm), (vii) Overall mass transfer coefficients of the gas in the carrier gas ($K_G$, cm/sec) and in the liquid water ($K_L$, cm/sec), (viii) Gas ($k_G$, cm/sec) and the liquid ($k_L$, cm/sec) film transfer coefficients, (ix) Gas ($r_G$, sec/cm) and liquid ($r_L$, sec/cm) phase resistances for the transfer of the pollutant to the water, (x) Thickness of the stagnant film in the liquid phase ($z_L$, cm).

The setup for the experiment which is used for the above-mentioned parameters is described. The only difference is an additional gas injector installed at the gas-liquid interface (Fig. 6). The procedure of the experiment is also identical from the previous.

## Conclusion

The limitation of RF-GC methodologies is that the substance that being use must be volatile so that a finite fraction of its distribution in the gaseous phase can be observed. Thus for the liquid under study especially organic, volatility is rarely adequate if the molecular weight of the compound exceeds 500 g/mol. Even though by increasing the temperature up to 300 °C can improve the vitality of the liquid, but the acts may leads on decomposition of the matter. It is believed that in

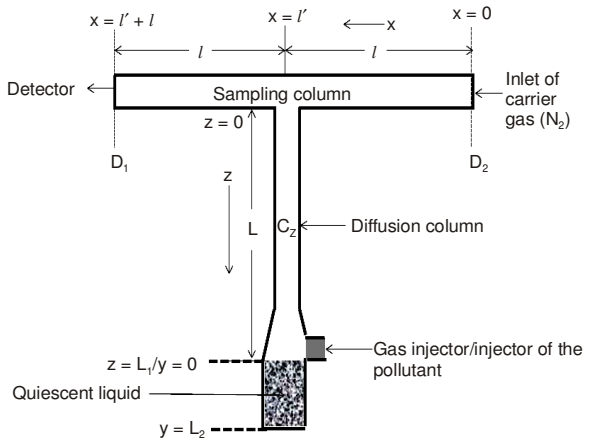


Fig. 6. Apparatus of the reversed-flow gas chromatography technique, for measuring the flux of gases across the air-water interface

case of the monolayer formation on the gas-liquid interface, there is need a further investigation on the pattern of distribution of surfactants on the surface of liquid by using BAM imager[44] in order to evaluate the distribution of monolayer on the liquid-gas interface. Furthermore, there is also needed of this method to be extended so that it can be applied to the environment analysis rather than become a dry subject by only collecting the data in the laboratory without any application to the environment. Since most of the cases the RF-GC deals with the pure liquids without any application of real world samples. The authors suggest that the set up for the RF-GC should be stretched forward so that the methodology can handle several samples at the same times. Plus, the researchers in this area should come out with solution on how to shorten the analysis time of this method since it requires at least 5 h and 40 min even though the sample peaks will become constant at 130-190 min after the first reversal. Since the FSG only applicable to linear molecules, the authors hope that in future this methodology could cater branched molecules, double bond and triple bond as well as aromatic compounds. Due to insufficient available experiment data, FSG could not offer the special atomic diffusion volumes for F, Br and I thus this will open the door for the new research in this particular area[45].

## ACKNOWLEDGEMENTS

The authors would like to thank Malaysian Agricultural Research and Development Institute (MARDI) and Bright Sparks Unit, Skim Biasiswazah Universiti Malaya for scholarship and financial assistance. The work was also supported by a Postgraduate Research Grant (PPP) No. PG067-2013A from Institute of Research Management and Monitoring (IPPP), Universiti Malaya. The author wants to dedicate their appreciation to the staff from the Library, University of Malaya for helping to provide some of the articles.

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Sains Malaysiana 43(12)(2014): 1915–1925

# Establishment of Physicochemical Measurements of Water Polluting Substances via Flow Perturbation Gas Chromatography

(Menentusahkan Tentu-ukur Juzuk Fiziko-kimia Bahan-bahan yang Mencemarkan Air Melalui Kromatografi Gas Aliran Terganggu)

H.H. MOHAMMAD*, SHARIFUDDIN MOHD ZAIN, RASHID ATTA KHAN & KHALISANNI KHALID

ABSTRACT

*Spillage of water polluting substances via industrial disaster may cause pollution to our environment. Thus, reversed-flow gas chromatography (RF-GC) technique, which applies flow perturbation gas chromatography, was used to investigate the evaporation and estimate the diffusion coefficients of liquid pollutants. Selected alcohols (99.9% purity) and its mixtures were used as samples. The evaporating liquids (stationary phase) were carried out by carrier gas-nitrogen, 99.9% purity (mobile phase) to the detector. The findings of this work showed the physicochemical measurements may vary depending on the composition of water and alcohol mixtures, temperature of the mixtures, as well as the types of alcohol used. This study implies that there is a variation in the results based on the concentration, types and temperature of the liquids that may contribute in the references for future research in the area of environmental pollution analysis.*

*Keywords: Alcohol mixtures; evaporation rates; liquid-gas interphase; liquid pollutants; spillage; vapour pressure*

ABSTRAK

*Limpahan bahan-bahan pencemaran melalui bencana industri boleh menyebabkan pencemaran kepada alam sekitar kita. Oleh itu, teknik gas kromatografi aliran berbalik (KTAB) yang mengaplikasikan teknik kromatografi gas aliran terganggu digunakan bagi menentu ukur kadar penyejatan dan menganggar pekali resapan bahan-bahan pencemar. Alkohol terpilih (99.9% darjah kepekatan) dan campuran telah digunakan sebagai sampel. Cecair menyejat (fasa penyebaran) telah diangkut oleh gas pengangkut iaitu nitrogen, 99.9% ketulenan (fasa persampelan) ke pengesan. Keputusan kajian ini menunjukkan ukuran fiziko-kimia mungkin berbeza bergantung kepada komposisi air dan alkohol di dalam campuran, suhu campuran dan jenis alkohol yang digunakan. Kajian ini menunjukkan bahawa terdapat perubahan keputusan berasaskan kepada kepekatan, jenis alkohol serta suhu campuran kajian, dan ia boleh menyumbang kepada rujukan untuk kajian akan datang dalam bidang analisis pencemaran alam sekitar.*

*Kata kunci: Campuran alkohol; cecair pencemar; fasa cecair-gas; kadar penyejatan; tekanan wap; tumpahan*

## INTRODUCTION

A substance or energy that enters the environment from different sources and has undesired effect or adverse effects on the usefulness of a resource is classified as pollutants. Pollutants from the atmosphere in the form of gaseous can diffuse into seawater by slow diffusion process that occurs in the air-water interphase. Pollution caused by alcohol is not a new phenomenon in the 21st century. The problem has increased and recognized more widely, simultaneously with the industrialization and growth of urban populations. The recent reported industrial accident of methanol spillage makes the study significant on the impact of alcohol to the environment (Mohammad et al. 2013). Evaporation emerges as an important process that happens in the air-water interphase and thus, encourages us to contribute to this particular field by acquiring data that can benefit the environmental researchers in the future. As a result, rate coefficients and diffusion coefficients in the gas phase play a major contribution on the transfer of pollutants from the air into water or vice versa.

There are two main categories of measuring the rate of evaporation in organic compounds, as reported in previous studies (Gavril et al. 2006), which involves the measurement of weight gain in vapour adsorbent above the liquid surface (Dilling 1977; Dilling et al. 1975; Mackay & Leinonen 1975; Mackay & Wolkolf 1973) and the rate of liquid loss into the moving gas stream flowing horizontally above the liquid surface (Beverley et al. 1999; Rusdi & Moroi 2004). The former allows the measurement of evaporation rates across a stagnant gas phase, while the latter measures the evaporation rates in perturbation gas flow. Most of the methods only measure the relative evaporation rates and evaporation halftimes which cannot portray the real physical properties of the evaporating organic compounds (Gavril et al. 2006).

Determination of the diffusion coefficients is really important for the area of basic and advanced research in engineering, as well as in chromatography (Karaiskakis & Gavril 2004). The data from the measurement of diffusion coefficient play a major role in the design of the reactors

since the interaction between gas phases is involved. On the other hand, diffusion is also important in chemical reaction and should be considered when one wants to construct a column for chromatography purposes. Besides, diffusion is also applicable in the field of atmospheric chemistry, combustion science, studies of indoor air pollution and atmosphere-biosphere interaction (Karaiskakis & Gavril 2004). Diffusion is also important to investigate the major factors in chromatography, which is peak broadening (Grushka & Maynard 1972; Karaiskakis & Gavril 2004). Thus, the reliability and accuracy of diffusion coefficient is vital to proof the theory in chromatography.

Fuller-Schettler-Giddings (FGS) equation is used for this experiment because it is an easily applied method for determining binary gas-phase diffusivities. They successfully developed a successful equation in which atomic and structural volume increments and other parameters were obtained by a nonlinear least squares analysis of 153 different binary systems (340 measurements) (Fuller et al. 1966; Karaiskakis & Gavril 2004). The measurements show the best average percentage accuracy (3.40%) in predicting binary gas-phase diffusivities as compared with other methods (cf Table 2 of (Karaiskakis & Gavril 2004)) and provide the best practical combination of simplicity and accuracy.

The idea of gas chromatographic method with periodic change (reversal) of the carrier gas flow (RFGC), which is related to the stopped-flow gas chromatography (SFGC) based on the works of Phillips et al. (1967) was proposed in 1980 by Katsonas (Karaiskakis et al. 1982). Initially, the RFGC method was designed for the measurement of the kinetic parameters of chemical reactions on the surface of the adsorbent-catalyst in chromatographic column-reactors (Karaiskakis et al. 1982). However, subsequently, the application of this method was greatly extended and RFGC was used to investigate the physiochemical properties of samples, such as the rate of coefficients (Karaiskakis & Katsanos 1984; Khalid et al. 2012), diffusion coefficients (Atta et al. 2002; Karaiskakis & Katsanos 1984; Khalid et al. 2011), mass transfer coefficients (Gavril & Karaiskakis 1997; Karaiskakis et al. 1986; Katsanos et al. 1988), activity coefficients (Agathonos & Karaiskakis 1989a, 1989b; Katsanos et al. 1985) and kinetic study of oxygen adsorption over supported catalysts (Dimitrios et al. 2012). Furthermore, this methods is also applied in separation for the growth phases of microbes (Lainioti et al. 2010) and surface studies (Gavril 2010; Metaxa et al. 2009).

The evaporation of pure liquids, as well as liquid mixtures has been studied in the past utilizing RF-GC (Karaiskakis & Katsanos 1984; Khalid et al. 2012; Mohammad et al. 2013). Previous works have intensively focused on the determination of the physiochemical measurement of the pure liquid pollutant while the current work, on the other hand also tries to investigate the effect of alcohol at different concentrations by using the same methodologies (Karaiskakis & Katsanos 1984; Khalid et al. 2011; Mohammad et al. 2013). There are quite a number of research studies on the evaporation of a binary low molecular weight alcohol mixture. Furthermore, studies on the evaporation rate and diffusion rate of low molecular weight alcohol are rare in literature. The aim of the present work were to investigate the effects of concentration of alcohol mixtures, the temperature being imposed, as well as the type of alcohol that influences the rate coefficients for evaporation and diffusion coefficients of that particular alcohol in the water environment.

## Materials and Methods

### Chemicals

The alcohols used (methanol, ethanol, 1-propanol and 1-butanol) were purchased from Merck (Kuala Lumpur, Malaysia). The gases were purchased from MOX (Kuala Lumpur, Malaysia), which comprised the carrier gas; nitrogen of 99.99% purity, as well as the fuel gases for the FID; hydrogen of 99.99% purity and compressed air.

### Procedures

The instruments used and the experimental procedures conducted are described (Karaiskakis & Katsanos 1984; Khalid et al. 2012; Mohammad et al. 2013). Reversed-flow gas chromatography (RF-GC) system, which is based on modified commercial gas chromatograph, comprises of six-port valve, sampling and diffusion columns and flame ionization detector (FID). A conventional gas chromatograph (Series GC-14B, Shimadzu, Japan) with an FID contained in its oven with two sections of *l*' and *l* in stainless-steel chromatographic column (57 + 57 cm × 4 mm I.D.), empty of any chromatographic material, is shown in Figure 1. The previous work had used the FID since its response factor was equal to unity, which definitely gives one to one response to the solute vapour in the sampling column (cf. Figure 1) during the sampling process (Katsanos et al. 1985).

The carrier gas supply and the detector via a six-port valve were connected to the sampling column via $D_1$ and $D_2$. The selection of nitrogen as the carrier gas was just because the gas accounts for 78% by volume of the air we breathe as dry atmosphere are mainly consists of nitrogen, oxygen and argon (> 99.9%), while carbon dioxide, krypton, neon, helium and xenon only contribute 0.1% (States & Gardner 2000). Furthermore, the problem of ethanol being a hygroscopic and easily absorbs moisture from the air, which arise from the previous study can be solved if nitrogen is used as the carrier gas, as manifested in previous investigations (O'Hare & Spedding 1992; O'Hare et al. 1993). The absorption rates of water by ethanol from the air has led to increased scatter in the pure ethanol data (O'Hare & Spedding 1992) even though the absorption rates are considered small in comparison with the evaporation rates. The fact directly indicates that nitrogen plays a major role in the atmosphere of air, plus the gas itself is non-reactive, easy to obtain and can be

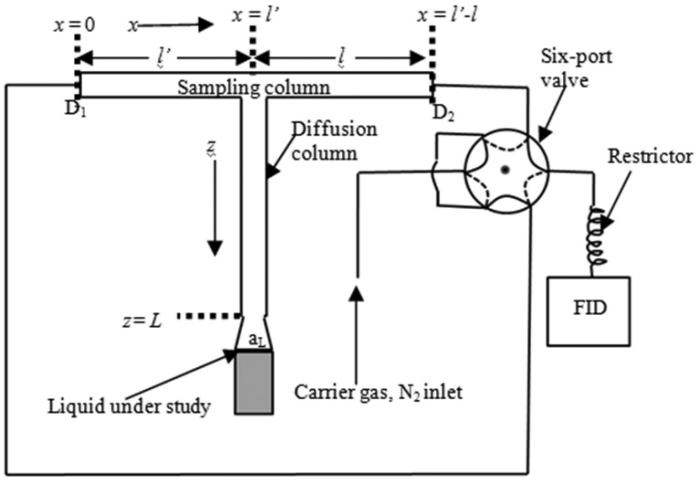


FIGURE 1. The set-up of reversed-flow gas chromatography technique for measuring rate coefficients and diffusion coefficients of water polluting substances

purchased at a reasonable cost (Goodman & Tipler 2009). By choosing the former gas as carrier gas, our work is proven to be significant for the environmental application to investigate the impact of liquid pollutants for studies on the environment.

The middle of the sampling column, $l' + l$ was connected perpendicularly at its upper end with a stainless steel diffusion column of length $L$ (28.5 cm × 4 mm I.D.). A 0.25 in. Swagelok tee union was used for the connection at the T-junction $x = l'$. A 2 cm tube containing 4 $cm^3$ of a pure liquid or a liquid mixture was connected to the lower end of the diffusion column, $L$ by Swagelok 0.25 in. union. The sampling cell, which consists of diffusion column and sampling column, was placed in the oven. The restrictor was placed before the detector to curb the flame of FID being extinguished when the perturbation process of the carrier gas was being carried out. The pressure drop along the sampling column, $l' + l$ was negligible. The temperature for the studies was restricted in the range of 313.15-373.15 K and the volumetric carrier gas flow-rate, was 1.00 $cm^3\ s^{-1}$.

After placing the glass tube containing liquid polluting substance, all joints in the sampling cell were tested with liquid leak detector for any leakage. Any formation of bubbles indicated that there was leakage at that particular joint. The automatic six-port valve was activated via LabSolutions CS software by Shimadzu from Personal Computer (PC) once the monotonously rising concentration-time (μV/s) curve for the vapour of the liquid mixture appeared on the monitor after a long time. The detector and PC were connected via CBM-102 Bus Module integrator. The sampling process was started by reversing the flow of carrier gas for an exact time period of 6 s. The reversal period was ensured to be shorter than the time in both sections $l'$ and $l$. When the carrier gas flow was restored in its original direction, sample peaks like those in Figure 2, which 'seat' on the baseline of the curve, were recorded, corresponding to various times $t_0$ from the beginning of the experiment. The theoretical basis and the calculation of evaporation rates, $K_G$ and diffusion rates, $D$ have been discussed intensively in the previous papers (Karaiskakis & Katsanos 1984; Khalid et al. 2012). Readers can always consult those papers if they are interested in the theoretical part of the current work.

## QA/QC OF RF-GC METHODS

The uncertainty in the determination of rate coefficients for evaporation mostly depends on the accuracy of the temperature control. The uncertainty of the chromatograph oven is ± 0.1 K for all experiments. The error in the determination of the diffusion coefficient may come from the measurement of the diffusion column, $L$. Since $D$ is proportional to $L^2$ (Gavril et al. 2006; Karaiskakis & Gavril 2004), small error while measuring the length of the column may contribute to the inaccuracy of the diffusion coefficients determination. We measured the column, $L$, directly and used a solute of accurately known for the diffusion coefficients in the given carrier gas (such as $C_2H_6O$ in $N_2$[23]) and carry out a calibration experiment for $L$. The value of $L$, which was determined at 28.5 cm, was used to estimate unknown diffusion coefficients based on the data from the previous work (Khalid et al. 2012) (c.f. rate coefficients for evaporation and diffusion coefficients values for methanol and 1-propanol (100% *v/v*) in Table 1). The determination of the evaporation rate depends also on the accuracy of the length of the diffusion column, $L$.

The nitrogen gas that was used in this experiment was filtered via carrier gas trap and filter (Z-Pure Glass Indicating Moisture Trap, CRS, USA) so that there was no moisture carried in the carrier gas. Furthermore, after running a particular sample, for example, 90% *v/v* methanol, the experiment was run with an empty bottle by increasing the temperature of the column up to 200°C in order to eliminate any dead volumes at any column junctions of the previous sample. This was to ensure that the columns were empty of any solute remaining from the

TABLE 1. The rate coefficients for the evaporation of the alcohol component at various volume percent (% *v*/*v*) from alcohol-water mixtures, and diffusion coefficients of the alcohol vapour into nitrogen at 1 atm pressure

| Alcohol | T (K) | $\dot{V}$ ($cm^3 s^{-1}$) | Volume percent (% *v*/*v*) | $10^2 K_G$ ($cm\ s^{-1}$) | | | $10^3 D$ ($cm^2 s^{-1}$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Present work | Reference 1 | Reference 2 | Present work | Reference 1 | Theoretical | Precision[#] (%) | Accuracy (%) |
| Methanol | 313.15 | 1.00 | 100 | 96.69 ± 0.20[a] | 140.87 ± 0.11 | 3.30[b] | 181.86 ± 0.04[a] | 184.30 ± 0.70 | 184.31 | 1.34 | 1.35 |
| | | | 95 | 47.10 ± 0.13[a] | - | - | 182.86 ± 0.04[a] | - | 184.31 | - | 0.80 |
| | | | 90 | 61.91 ± 0.15[a] | - | - | 181.86 ± 0.03[a] | - | 184.31 | - | 0.20 |
| Ethanol | 313.15 | 1.00 | 100 | 175.58 ± 0.07[a,*] | 175.58 ± 0.07 | 2.79[c] | 140.40 ± 0.09[a] | 140.04 ± 0.90 | 140.30 | 0.00 | 0.06 |
| | | | 95 | 70.92 ± 0.15[a] | - | - | 113.28 ± 0.07[a] | - | 140.33 | - | 5.29 |
| | | | 90 | 47.51 ± 0.89[a] | - | - | 146.88 ± 0.09[a] | - | 140.33 | - | 4.46 |
| 1-propanol | 313.15 | 1.00 | 100 | 190.94 ± 0.15[a,*] | 190.94 ± 0.15 | 3.64[d] | 116.90 ± 0.02[a] | 119.90 ± 0.20 | 116.90 | 2.57 | 0 |
| | | | 95 | 70.79 ± 0.16[a] | - | - | 116.21 ± 0.01[a] | - | 116.94 | - | 0.63 |
| | | | 90 | 74.12 ± 0.04[a] | - | - | 116.31± 0.01[a] | - | 116.94 | - | 0.53 |
| 1-butanol | 313.15 | 1.00 | 100 | 54.51 ± 0.19[a] | 208.68 ± 0.08 | 2.68[e] | 101.00 ± 0.03[a] | 102.00 ± 0.50 | 102.03 | 0.98 | 1.02 |
| | | | 95 | 50.23 ± 0.09[a] | - | - | 101.55 ± 0.03[a] | - | 102.03 | - | 0.48 |
| | | | 90 | 61.77 ± 0.15[a] | - | - | 101.71 ± 0.01[a] | - | 102.03 | - | 0.31 |

[a]Uncertainty obtained from the standard error of the $K_G$ and $D$ values from the slopes of the linear plots of (20) and (21) of (Karaiskakis & Katsanos 1984), respectively. Number of the observations being made for each point, $n$=3

*This measurement is done by using 0.5 $cm^3$ solute in the glass bottle while the rest of the experiments, the volume of the solute was 4.0 $cm^3$. The former volume of the solute being used to calibrate the diffusion column, $L$. (cf. QA/QC OF RF-GC METHODOLOGY section)

Reference1 : (Khalid et al. 2012)

Reference 2 : The rate coefficient for evaporation is measured at 322.5 K[b], 336.8 K[c], 342.3 K[d], and 358.1 K[d], respectively. The length of diffusion column, $L$ = 116.2 cm with the flow of the carrier gas is in the range 0.290-0.674 $cm^3\ s^{-1}$ is used for the experiment.(Karaiskakis & Katsanos 1984)

[#] Precision has been defined as ( $|D_{\text{present work}} - D_{\text{reference/literature}}|/D_{\text{present work}}$)*100 (Karaiskakis & Gavril 2004)

previous experiment. We ensured that the chromatogram achieved a stable baseline before conducting the reversal process. Plus, every rate coefficients data for this experiment were compared with the FSG theoretical value and one finds that the values' accuracy was less than 5%, which is considered as accepted tolerance value.

## Results and Discussion

In the present paper, the rate coefficients for the evaporation of the liquid mixtures methanol-water, ethanol-water, 1-propanol-water and 1-butanol-water, as well as the diffusion of those liquids into carrier gas nitrogen, were determined.

Table 1 shows the results obtained with all the pure alcohol, as well as their mixtures being studied at constant temperature and various alcohol concentrations. The rate coefficient for evaporation of the current work is listed in the fifth column of Table 1. Previous works (Karaiskakis & Katsanos 1984; Khalid et al. 2012) measured the rate coefficients for evaporation for pure liquid alcohol in carrier gas helium and nitrogen, respectively.

Comparison of the results for the evaporation of pure ethanol and 1-propanol 100% *v/v,* with the literature, shows relatively good accuracy. We used the same volume of ethanol and 1-propanol, which was 0.5 $cm^3$ as used in the previous work (Khalid et al. 2012) in order to calibrate the diffusion column, *L,* whereby the procedure is elaborated in the previous section. For the rest of the experiment, we used 4.0 $cm^3$ of alcohol to measure the rate coefficient for evaporation and the diffusion coefficient of alcohols into carrier gas nitrogen. The rate coefficient for evaporation calculated for methanol and 1-butanol was less than the amount used in the previous work (Khalid et al. 2012) because the liquid coverage area, $a_L$ for both experiments was different (cf. Figure 1). When less liquid was poured in the glass bottle, the coverage area of the liquid was bigger since the liquid was deposited at the bottom of the bottle. In the present work, we used 4.0 $cm^3$ of alcohol and the liquid almost filled the whole bottle and the liquid level was at the neck of the bottle, which is shown in Figure 1. Thus, the liquid coverage area, $a_L$ was smaller as compared to when less liquid was poured into the bottle.

On the other hand, when all the $K_G$ values of pure alcohol found in the work was compared with the literature, as shown in the seventh column of Table 1 (Karaiskakis & Katsanos 1984), the values of $K_G$ for the former was higher than the latter. This was due to the bigger size of carrier gas nitrogen's molecules, employed in this work, compared with carrier gas helium, used in the literature work. The variation in $K_G$ value seemed to be logical, as the temperature conditions, as well as carrier gas were different in the literature. Otherwise, the values of $K_G$ were higher for the former than the latter. Besides, the value of $K_G$ found in this work for pure alcohols was between the afore-mentioned literature values (Karaiskakis & Katsanos 1984; Khalid et al. 2012).

This phenomenon was described in Figure 6. Figure 6 shows the attractive force between the alcohol's molecules at the interface of liquid bulk and the vapour phase of the alcohol. When the molecules were exposed to the larger liquid coverage area, $a_L$ more molecules were exposed at the interface and increased the probability of the molecules to be ejected from the liquid bulk (Birdi et al. 1989; Jozsef 2009; Rowan et al. 1995). The attractive forces between the molecules at the interface and the molecules in the liquid bulk became weaker and the molecules at the interface escaped into vapour phase (Davies & Rideal 1961). Thus, the rate coefficient for evaporation of methanol and 1-butanol was higher in the larger liquid coverage area, $a_L$.

The diffusion coefficients were compared with those calculated theoretically using Fuller-Schettler-Giddings (FSG) equation (cf. supplementary material) (Fuller et al. 1966), permits the calculation of the method's accuracy, which is defined as,

$$\text{Accuracy } (\%) = [(D_{\text{present work}} - D_{\text{theoretical}})/D_{\text{present work}}]*100. \quad (1)$$

The results are tabulated in the last column of Table 1. The table shows that the $K_G$ values increased with increasing the alcohol's volume percent (% *v/v*) generally. The evaporation rate of the alcohol increased as the alcohol's volume percent (% *v/v*) increased, as pictured in Figure 3. The results applied for all alcohols for this study, except for 1-butanol. The equilibrium of liquid-vapour phase is established in the diffusion column (cf. Figure 1), between 130-330 min, since the intensity-time graph (cf. Figure 2) reaches plateau in this period. The fact that 1-butanol had negative gradient, as depicted in Figure 3 (decreasing evaporation rate as composition of 1-butanol in water is increasing) because 1-butanol possessed the lowest vapour pressure as compared with others. Thus, there was a small deviation of evaporation in pure 1-butanol and its mixture (90-95% *v/v* in water). The previous study also showed that the evaporation of the alcohol components, comprising a binary mixture with water, could be predicted in terms of vapour pressure (O'Hare & Spedding 1992). The investigators believe that the vapour pressure acted as a driving force in a similar way as the pure component (alcohol) evaporation. The vapour pressure exerted by the alcohol became significant as compared to the water component in the mixture in the range of 30-100% *w/w*.

The rate coefficients for the evaporation of the alcohols (90% *v/v*) at various temperatures, ranging from 313.15-373.15 K, as well as the diffusions coefficients of the alcohol vapours into nitrogen at these temperatures, are compiled in Table 2. The conclusion can be drawn from this table is that the $K_G$ values increased with the increase of the temperature in accordance with the Arrhenius equation (Karaiskakis et al. 1986), as depicted in Figure 4, when the $K_G$ values are plotted against reciprocal of their temperatures. From the Arrhenius equation,

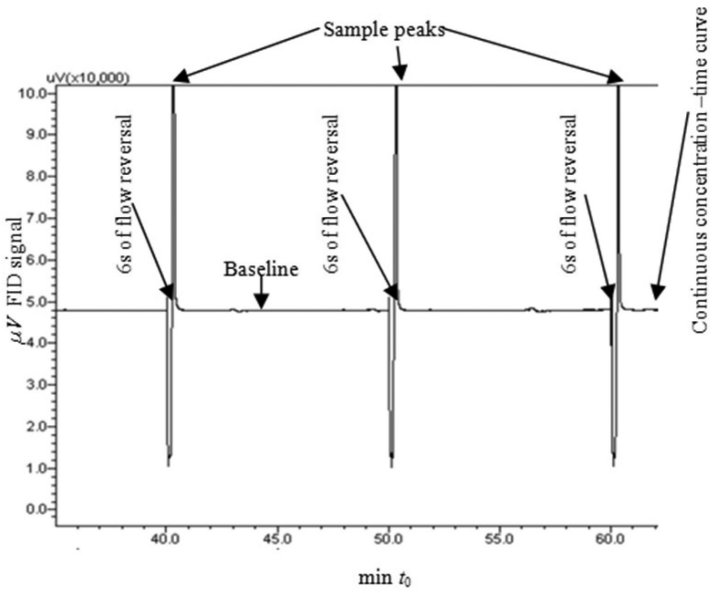


FIGURE 2. Three sample peaks for the diffusion of liquid mixture vapours into carrier gas nitrogen at 323.15 K and 101325 Pa (volumetric flow rate = 1 $cm^3min^{-1}$) extracted from a reversed-flow chromatogram

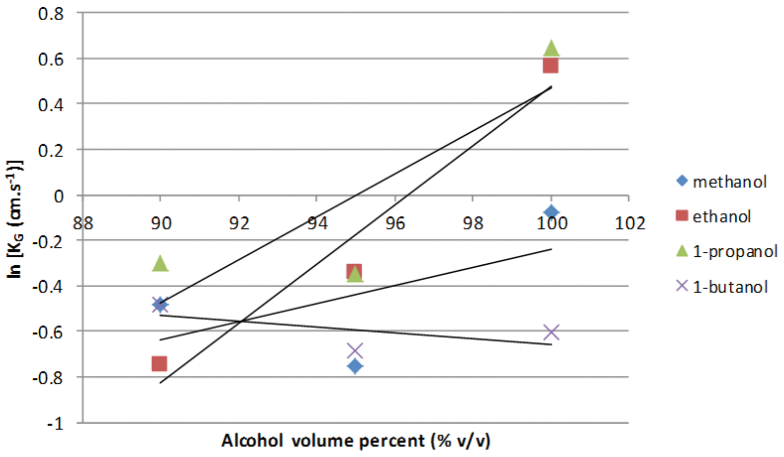


FIGURE 3. Volume percent (% *v*/*v*) dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures at 313.15 K

$$\ln k = \ln A - \frac{E_a}{RT}, \qquad (2)$$

where $k$ is the rate coefficients for evaporation (cm $s^{-1}$); $E_a$ is the activation energy of the alcohol (J $mol^{-1}$); $T$ is temperature of the liquid (Kelvin); $R$ is the constant (8.3145 J $mol^{-1}$ $K^{-1}$) and $A$ is an arbitrary constant, one can calculate the activation energy, $E_a$ of the selected alcohol. Previous works (Karaiskakis et al. 1986; Khalid et al. 2012) have calculated the activation energy, $E_a$ of the pure alcohols and they found that the values were smaller than 40 kJ $mol^{-1}$(Katsanos 1988). This was expected since $K_G$ values were rate coefficients for evaporation, which is a physical phenomenon (Karaiskakis et al. 1986). Besides, we obtained a linear Arrhenius plot with negative slope, which portrays that the activation energy, $E_a$ of the selected alcohols changed with temperature (Khalid et al. 2012) and the type of alcohols. The differences of the slope in the plot were expected since different types of alcohols possess different activation energy, $E_a$. The steeper the slope means the higher the activation energy and the stronger the temperature dependence of the rate coefficients for evaporation of one particular alcohol (Peter & De 2006). Based on the plot in Figure 4, methanol (90% *v*/*v*) has the steepest slope among the alcohols, which indicates that methanol (90% *v*/*v*) possesses the highest activation energy and the strongest temperature dependence of the rate coefficients for evaporation.

The temperature dependence of the rate coefficients for evaporation can be described as follows: The kinetic energy, i.e. the tendency of the alcohol's molecules to escape from the liquid surface is governed by the temperature. A certain fraction of the molecules possess

TABLE 2. The rate coefficients for the evaporation of the alcohol component from alcohol-water mixtures at constant alcohol volume percent (% *v/v*) and various temperatures and diffusion coefficients of the alcohol vapour into nitrogen at 1 atm pressure

| Alcohol | Volume percent (% v/v) | $\dot{V}$ ($cm^3\ s^{-1}$) | T (K) | $10^2 K_G$ ($cm\ s^{-1}$) | $E_a$ ($kJ\ mol^{-1}$) | $10^3 D$ ($cm^2 s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Present work | Theoretical | Accuracy (%) |
| Methanol | 90 | 1.00 | 313.15 | 61.91 ± 0.15[a] | 36.4 | 181.86 ± 0.03[a] | 184.31 | 0.20 |
| | | | 323.15 | 138.81 ± 0.46[a] | | 198.13 ± 0.04[a] | 194.74 | 1.71 |
| | | | 333.15 | 142.34 ± 0.88[a] | | 208.79 ± 0.18[a] | 205.41 | 1.62 |
| Ethanol | 90 | 1.00 | 313.15 | 47.51 ± 0.89[a] | 27.7 | 146.88 ± 0.09[a] | 140.33 | 4.46 |
| | | | 323.15 | 71.01 ± 0.12[a] | | 149.17 ± 0.01[a] | 148.27 | 0.50 |
| | | | 333.15 | 94.49 ± 0.07[a] | | 159.87 ± 0.02[a] | 156.39 | 0.84 |
| | | | 343.15 | 141.77 ± 0.44[a] | | 167.43 ± 0.01[a] | 164.70 | 1.62 |
| | | | 353.15 | 170.68 ± 0.07[a] | | 172.73 ± 0.01[a] | 173.19 | 0.26 |
| | | | 363.15 | 199.44 ± 0.12[a] | | 180.12 ± 0.02[a] | 181.86 | 0.84 |
| 1-propanol | 90 | 1.00 | 313.15 | 74.12 ± 0.04[a] | 10.9 | 116.31± 0.01[a] | 116.94 | 0.53 |
| | | | 323.15 | 83.36 ± 0.02[a] | | 123.65 ± 0.02[a] | 123.35 | 0.08 |
| | | | 333.15 | 92.17 ± 0.68[a] | | 130.03 ± 0.02[a] | 130.32 | 0.22 |
| | | | 343.15 | 104.40 ± 0.02[a] | | 138.37 ± 0.02[a] | 137.24 | 0.60 |
| | | | 353.15 | 125.61 ± 0.04[a] | | 143.12 ± 0.02[a] | 144.32 | 0.83 |
| | | | 363.15 | 126.58 ± 0.27[a] | | 150.70 ± 0.03[a] | 151.54 | 0.56 |
| 1-butanol | 90 | 1.00 | 313.15 | 61.77 ± 0.15[a] | 8.4 | 101.71 ± 0.01[a] | 102.03 | 0.31 |
| | | | 323.15 | 71.44 ± 0.19[a] | | 107.00 ± 0.02[a] | 107.80 | 0.75 |
| | | | 333.15 | 72.56 ± 0.04[a] | | 113.28 ± 0.01[a] | 113.71 | 0.37 |
| | | | 343.15 | 82.52 ± 0.03[a] | | 117.40 ± 0.01[a] | 119.75 | 2.00 |
| | | | 353.15 | 91.33 ± 0.02[a] | | 124.56 ± 0.01[a] | 125.92 | 1.09 |
| | | | 363.15 | 97.14 ± 0.09[a] | | 133.74 ± 0.02[a] | 132.22 | 1.13 |
| | | | 373.15 | 104.54 ± 0.12[a] | | 136.27± 0.03[a] | 138.66 | 1.75 |

[a]Uncertainty obtained from the standard error of the $K_G$ and $D$ values from the slopes of the linear plots of (20) and (21) of (Karaiskakis & Katsanos 1984), respectively. Number of the observations being made for each point, $n$=3

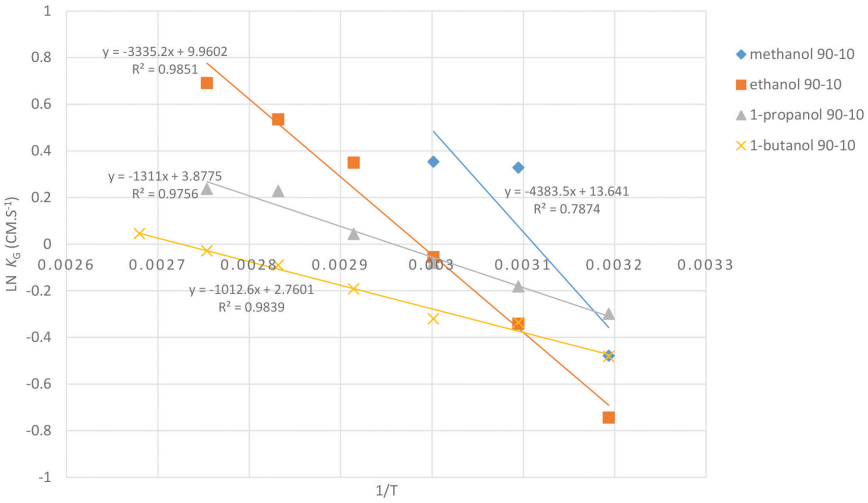


FIGURE 4. Temperature dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures in volume percent (% *v*/*v*)

enough kinetic energy to overcome the forces of attraction of the surrounding molecules and to escape from the surface of the liquid at each temperature (Jozsef 2009). When higher temperature is exposed to the alcohols, the alcohol's particles with higher average kinetic energy will populate on the surface of the liquid. Some particles will have higher kinetic energy than the average kinetic energy and tends to escape from the liquid surface, while some others possess lower kinetic energy than the average and remains on the liquid surface.

The accuracy of the diffusion coefficients of the methanol 90% *v*/*v* into nitrogen gas were found to be less than 2% and this means that the experimental values of the coefficients are closed to the theoretical values predicted by Fuller-Schettlar-Giddings (FSG)(Fuller et al. 1966). To the best of our knowledge, only Khalid et al. (2012) managed to get less than 0.2% in all the diffusion coefficients measurement of organic liquid using the reversed-flow gas chromatography methods.

Table 3 shows the rate coefficients for the evaporation of the alcohol component from alcohol-water mixtures at constant alcohol volume percent (90% *v*/*v*) and various types of the low molecular weight alcohol vapour into nitrogen at 1 atm pressure. From the table, we can conclude that the evaporation rate of the alcohol increased as the molecular weight of the alcohol decreased, as depicted by the graph in Figure 5. Since there was no other works measuring the diffusion coefficients of methanol at 90% v/*v*, the value of the coefficients were compared with the theoretical calculation from the FSG equation and the accuracy of the coefficients was less than 2% for this case. The results in the fifth column show that the evaporation process was highly dependent on the structure, the molecule weight of the alcohol, as well as the concentration percentage of the selected alcohol. The light molecule and high volatile liquid were easier to evaporate compared with the heavier ones (Hofmann 1932). The present experiment also supports the previous study (Brown et al. 1969; Hu et al. 2010; O'Hare et al. 1993), which concludes that ethanol seems to possess lower evaporation rates as compared to 1-propanol due to the hydrogen bonding that makes the hydroxyl ion of ethanol being 'trapped' in a fluctuation clathrate structure. The current study only focused on the straight chain, low molecular weight alcohol as evaporate liquid since it is widely used as bio fuel in vehicles (Cheng & Timilsina 2011). Thus, the rate of coefficient for evaporation increased based on the following trends:

1-butanol < Ethanol < 1-propanol < Methanol

Rate coefficient for evaporation increases

## CONCLUSION

The findings provide a useful data for estimating the evaporation, as well as diffusion rates of water polluting substances at different concentration, temperatures and types of alcohols being used towards environmental science application. The accuracy of diffusion rates calculated from the experiments based on FSG equation with no exception is better than 5% in all cases and falls between the diffusion coefficients values calculated by the previous work. The uniqueness of the method is because of its simplicity which makes the measurement of physicochemical much simpler since the time taken to acquire the data was less than 3 h. Furthermore, this method enables us to measure the rate coefficients, as well as the diffusion coefficients of the liquids simultaneously. Future work should focus on retarding the evaporation of the dangerous polluted liquid to the environment since it may cause devastating effect on the human health.

TABLE 3. The rate coefficients for the evaporation of the alcohol component from alcohol-water mixtures at constant alcohol volume percent (% *v*/*v*) and various types of the low molecular weight alcohol vapour into nitrogen at 1 atm pressure

| Alcohol | T (K) | ($cm^3 s^{-1}$) | Volume percent (% v/v) | $10^2 K_G$ (cm $s^{-1}$) | $10^3 D$ ($cm^2 s^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| | | | | | Present work | Theoretical | Accuracy (%) |
| Methanol | 323.15 | 1.00 | 90 | 138.81 ± 0.46[a] | 198.13 ± 0.04[a] | 194.74 | 1.71 |
| Ethanol | 323.15 | 1.00 | 90 | 71.01 ± 0.12[a] | 149.17 ± 0.01[a] | 148.27 | 0.50 |
| 1-propanol | 323.15 | 1.00 | 90 | 83.36 ± 0.02[a] | 123.65 ± 0.02[a] | 123.35 | 0.08 |
| 1-butanol | 323.15 | 1.00 | 90 | 71.44 ± 0.19[a] | 107.00 ± 0.02[a] | 107.80 | 0.75 |

[a]Uncertainty obtained from the standard error of the $K_G$ and $D$ values from the slopes of the linear plots of Eqs. 20 and 21 of (Karaiskakis & Katsanos 1984), respectively. Number of the observations being made for each point, $n$=3

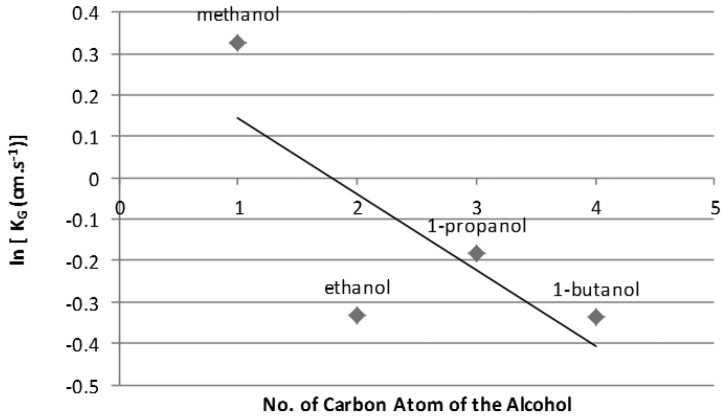


FIGURE 5. Types of alcohol dependence of $K_G$ for the evaporation of the alcohol from the alcohol-water mixtures at 323.15 K

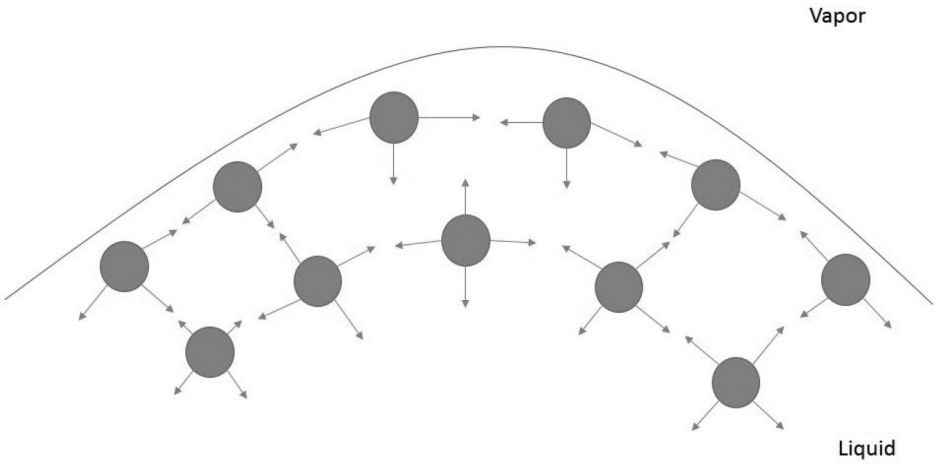


FIGURE 6. Attractive forces (represented by arrows) between alcohol's molecules (show as spheres) at the surfaces and in the interface of a liquid. (FIGURE 6 adapted from (Davies & Rideal 1961))

ACKNOWLEDGEMENTS

The authors would like to thank the Malaysian Agricultural Research and Development Institute (MARDI) and Bright Sparks Unit, Skim Biasiswazah Universiti Malaya for the scholarship and financial assistance. The work was also supported by a Postgraduate Research Grant (PPP) No. PG067-2013A from Institute of Research Management and Monitoring (IPPP), University of Malaya. The authors would like to dedicate a special thanks to the staff from the Department of Chemistry, Universiti Malaya for the technical support.

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Received: 6 December 2013
Accepted: 16 April 2014